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GUIDELINES FOR DEVELOPMENT OF A QUALITY ASSURANCE PROGRAM

REFERENCE METHOD FOR THE DETERMINATION OF SULFUR DIOXIDE IN THE ATMOSPHERE

RESEARCH TRIANGLE INSTITUTE

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1. Good operating practices
2. Directions on how to assess and qualify data
3. Directions on how to identify trouble and improve data quality.
4. Directions to permit design of auditing activities
5. Procedures for selecting action options and relating them to costs.

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GUIDELINES FOR DEVELOPMENT OF A QUALITY ASSURANCE PROGRAM

Reference Method for the Determination of Sulfur Dioxide in the Atmosphere

by

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PREFACE

Quality control is an integral part of any viable environmental monitoring activity. The primary goals of EPA's quality control program are to improve and document the credibility of environmental measurements. To achieve these goals, quality control is needed in nearly all segments of monitoring activities and should cover personnel, methods selection, equipment, and data handling procedures. The quality control program will consist of four major activities:

- Development and issuance of procedures
- Intra-laboratory quality control
- Inter-laboratory quality control
- Monitoring program evaluation and certification

All these activities are essential to a successful quality control program and will be planned and carried out simultaneously.

Accordingly, this fourth manual of a series of five has been prepared for the quality control of ambient air measurements. These guidelines for the quality control

of sulfur dioxide measurements in the atmosphere have been produced under the direction of the Quality Control Branch of the Quality Assurance and Environmental Monitoring Laboratory of NERC/RTP. The purpose of this document is to provide uniform guidance to all EPA monitoring activities in the collection, analysis, interpretation, presentation, and validation of quantitative data. In accordance with administrative directives to implement an agency-wide quality control program, all EPA monitoring activities are requested to use these guidelines to establish intralaboratory quality assurance programs in the conduct of all ambient air measurements for sulfur dioxide. Your comments on the utility of these guidelines, along with documented requests for revision(s), are welcomed.

All questions concerning the use of this manual and other matters related to quality control of air pollution measurements should be directed to:

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During the months ahead, a series of manuals will be issued which describe guidelines to be followed during the course of sampling, analysis, and data handling. The use of these prescribed guidelines will provide a uniform approach in the various monitoring programs which allows the evaluation of the validity of data produced. The implementation of a total and meaningful quality control program cannot succeed without the full support of all monitoring programs. Your cooperation is appreciated.

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ABSTRACT

Guidelines for the quality control of Federal reference method for sulfur dioxide are presented. These include:

1. Good operating practices
2. Directions on how to assess data and qualify data
3. Direction on how to identify trouble and improve data quality
4. Directions to permit design of auditing activities
5. Procedures which can be used to select action options and relate them to costs.

The document is not a research report. It is designed for use by operating personnel.

This work was submitted in partial fulfillment of Contract Durham 68-02-0598 by Research Triangle Institute under the sponsorship of the Environmental Protection Agency. Work was completed as of July 1973.

SECTION I INTRODUCTION

This document presents guidelines for implementing a quality assurance program for the manual (non-continuous) measurement of atmospheric sulfur dioxide by the pararosaniline method.

The objectives of this quality assurance program for the pararosaniline method of measuring atmospheric sulfur dioxide are to:

(1) provide routine indications for operating purposes of unsatisfactory performance of personnel and/or equipment,

(2) provide for prompt detection and correction of conditions which contribute to the collection of poor quality data, and

(3) collect and supply information necessary to describe the quality of the data.

To accomplish the above objectives, a quality assurance program must contain the following components:

(1) routine training and/or evaluation of operators,

(2) routine monitoring of the variables and/or parameters which may have a significant effect on data quality,

(3) development of statements and evidence to qualify data and detect defects, and

(4) action strategies to increase the level of precision in the reported data and/or to detect equipment defects or degradation and to correct same.

Implementation of a quality assurance program will result in data that are more uniform in terms of precision and accuracy. It will enable each monitoring network to continuously generate data that approach the highest level of accuracy attainable with the pararosaniline method.

This document is divided into four sections or chapters. They are:

Section I, Introduction - The introduction lists the overall objectives of a quality assurance program and delineates the program components necessary to accomplish the given objectives.

Section II, Operations Manual - The Operations Manual sets forth recommended operating procedures, instructions for performing control checks designed to give an indication or warning that invalid or poor quality data are being collected, and instructions for performing certain special checks for auditing purposes.

Section III, Supervision Manual - The Supervision Manual contains directions for 1) assessing sulfur dioxide data, 2) collecting information to detect and/or identify trouble, 3) applying quality control procedures to improve data quality, and 4) varying the auditing or checking level to achieve a desired level of confidence in the validity of the outgoing data. Also, monitoring strategies and costs as discussed in Section IV are summarized in this manual.

Section IV, Management Manual - The Management Manual presents procedures designed to assist the manager in 1) detecting when data quality is inadequate, 2) assessing overall data quality, 3) determining the extent of independent auditing to be performed, 4) relating costs of data quality assurance procedures to a measure of data quality, and 5) selecting from the options available the alternative(s) which will enable one to meet the data quality goals by the most cost-effective means. Also, discussions on data presentation and personnel requirements are included in this manual.

The scope of this document has been purposely limited to that of a field document. Additional background information is contained in the final report under this contract.

SECTION II OPERATIONS MANUAL

GENERAL

This operations manual sets forth recommended operating procedures for the colorimetric measurement of sulfur dioxide in the atmosphere using the non-continuous pararosaniline method. Quality control procedures and checks designed to give an indication or warning that invalid or poor quality data are being collected are written as part of the operating procedures and are to be performed by the operator on a routine basis. In addition, the performance of special quality control procedures and/or checks as prescribed by the supervisor may be required of the operator on certain occasions.

The accuracy and/or validity of data obtained from this method depends upon equipment performance and the proficiency with which the operator performs his various tasks. This measurement method from reagent preparation through sample collection, analysis, and data reporting is a complex operation. Presenting detailed instructions covering all alternatives has not been attempted in this document. Rather, general guidelines are presented with special emphasis on quality control checks and decision rules applicable to known problem areas. The operator should make himself familiar with the rules and regulations concerning the Reference Method as written in the Federal Register, Vol. 36, No. 84, Part II, April 30, 1971 (reproduced as the Appendix of this document for convenience of reference).

Instructions throughout this document are directed primarily toward a 24-hour sampling period with comments on 30-minute and 1-hour sampling periods when appropriate. Also, an auditing or checking level of 1 check out of every 14 sampling periods or once a calendar month, whichever occurs first, is used. Sampling period durations and auditing levels are subject to change by the supervisor and/or manager. Such changes would not alter the basic directions for performing the operation. Also, certain control limits as given in this manual represent best estimates for use in the beginning of a quality assurance program and are, therefore, subject to change as field data are collected.

It is assumed that all apparatus satisfies the reference method specifications and that the manufacturer's recommendations will be followed when using a particular item of equipment (e.g., spectrophotometer and wet test meter).

The sequence of operations to be performed during each sampling period is given in Figure 1. Certain operations such as reagent preparation and flow-rate calibration (when a rotameter is used as the flowmeter) are performed periodically. The remaining operations are performed during each sampling period. The operations are classified as presampling preparation, sample collection, sample analysis, and data processing. Each operation or step in the process is identified by a block. Quality checkpoints in the measurement process, for which appropriate quality control limits are assigned, are represented by blocks enclosed by heavy lines. Other

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PRESAMPLING PREPARATION

1. PREPARE OR OBTAIN OXIDANT-FREE DISTILLED WATER. PREPARE AND CHECK ABSORBING REAGENT.

2. CALIBRATE FLOWMETER/FLOW CONTROLLER (ROTAMETER/CRITICAL ORIFICE) AGAINST A STANDARD AS SCHEDULED.

3. SELECT PROPER ABSORBER FOR SAMPLING PERIOD OF INTEREST. CLEAN AND ASSEMBLE THE ABSORBER.

4. RECORD IDENTIFYING INFORMATION IN THE OPERATIONAL DATA LOG BOOK AND ON THE ABSORBER TUBE.

5. PREPARE ABSORBER FOR DELIVERY/SHIPMENT TO THE SAMPLING SITE.

SAMPLE COLLECTION

6. ASSEMBLE SAMPLE COLLECTION SYSTEM IF NECESSARY INSTALL ABSORBER AND CRITICAL ORIFICE INTO THE SAMPLING TRAIN.

7. PERFORM SYSTEM OPERATIONAL CHECKS AND RECORD ON THE SAMPLE RECORD SHEET.

8. AMBIENT AIR IS SAMPLED AT A FIXED FLOW RATE FOR THE DURATION OF THE SAMPLING PERIOD.

9. REMOVE THE EXPOSED ABSORBER FROM THE SAMPLING TRAIN, PREPARE THE SAMPLE FOR DELIVERY/SHIPMENT, OBSERVE AND RECORD ANY LOCAL CONDITIONS WHICH MIGHT AFFECT THE POLLUTION LEVEL.

SAMPLE ANALYSIS

10. CHECK ALL DOCUMENTATION UP TO THIS POINT FOR ACCURACY AND COMPLETENESS.

11. RECALIBRATE THE CRITICAL ORIFICE, IF USED, AS IN STEP 2. RECORD THE FINAL FLOW RATE IN THE FLOW-RATE CALIBRATION LOG BOOK.

12. PREPARE THE REAGENTS USED IN THE ANALYSIS OF SO_2 SAMPLES.

13. DEVELOP A CALIBRATION CURVE USING EITHER THE SULFITE OR PERMEATION TUBE METHOD.

14. MEASURE THE ABSORBANCE OF THE SAMPLE SOLUTION AT 548 nm.

DATA PROCESSING

15. PERFORM NECESSARY CALCULATIONS TO ARRIVE AT AN AVERAGE CONCENTRATION OF SO_2 IN $\mu g/m^3$ AT 25°C AND 760 mmHg FOR THE SAMPLING PERIOD.

16. RECORD CONCENTRATIONS AND IDENTIFYING DATA ON SAROAD FORM, ATTACH AUDIT DATA AND FORWARD FOR ADDITIONAL INTERNAL REVIEW OR TO USER.

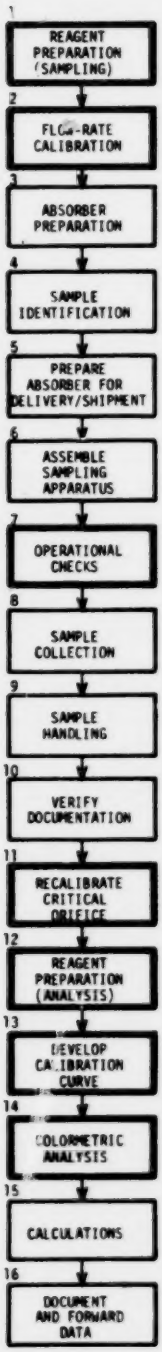

FIGURE 1. OPERATIONAL FLOW CHART OF THE MEASURING PROCESS

checkpoints involve go/no-go checks and/or subjective judgments by the operator with proper guidelines for decision-making spelled out in the procedures. *These operations and checks are discussed sequentially as one progresses step by step through the sequence of actions in Figure 1.*

The operator is responsible for maintaining certain records. Specifically, the following log books are maintained:

(1) Operational Data Log Book. Sample identification data, completed gas sample record sheets, and analysis results are filed or recorded in the operational data log book.

(2) Flow-Rate Calibration Log Book. Critical orifice or rotameter calibration data are recorded, dated and signed in this log book.

(3) SO_2 Calibration Log Book. Completed calibration curves and control sample measurement data are maintained in the calibration log book.

PRESAMPLING PREPARATION

Operations included in this classification are (1) preparation of absorbing reagent, flow-rate calibration, absorber preparation, sample identification, and preparation of the absorber and flowmeter (critical orifice) for shipment.

Reagent Preparation (Step 1)

In reagent preparation for sampling and analysis all chemicals should be ACS analytical reagent grade or better. Unless otherwise indicated, references to water implies distilled water free from oxidants. Only Class A volumetric glassware should be used. All weights should be made on an analytical balance sensitive to the nearest 0.1 mg, or better.

Distilled Water - Water must be free from oxidants. It should preferably be double-distilled from all glass apparatus. The purity of the water should be checked when first purchased/prepared and before preparing a batch of reagents for sampling or analysis.

Test for purity - Distilled water can be tested for purity from oxidants in the following manner.

(1) Add 0.20 mℓ of $KMnO_4$ solution (0.316 g/ℓ) to a mixture of 500 mℓ of the distilled water and 1 mℓ of H_2SO_4 in a stoppered bottle of chemically resistant glass.

(2) If the permanganate color (blue) does not disappear completely after standing for 1 hour at room temperature, consider the water suitable for use.

(3) If the permanganate does disappear, the water must be purified before using.

Purification procedure - Water failing the purity test can be purified as follows:

(1) Add one crystal each of potassium permanganate and barium hydroxide for each liter of distilled water.

(2) Redistill the water in an all-glass still.

(3) Perform the test for purity as described above.

(4) Repeat the purification procedure and the test for purity until the water checks pure.

This distilled water, free of oxidants, is used any time water is required in preparing reagents for sampling or analysis.

Storage of distilled water - Oxidant free water should at all times be protected from atmospheric contamination by storing in container made of material that has been proven to be resistant to solvation by, or reaction with, the water. Also, any tubing used during reagent preparation should be of high resistant material. Also, when removing water from the storage container the replacement air should be drawn through a vent guard (e.g., a drying tube filled with equal parts of 8-20-mesh soda lime, oxalic acid, and 4-8-mesh calcium chloride, each compound being separated from the other by a glass wool plug).

Absorbing Reagent - Prepare a batch of absorbing reagent as directed in Subsection 6.1.2 of the Appendix, page 113. The preparation and subsequent handling of the absorbing reagent should be carried out under a ventilation hood.

Reagent pH check - It is suggested that the pH of the absorbing reagent be checked with a pH meter and a glass electrode standardized in a buffer solution with a pH of about 4.5. If the weighings and volumetric measurements have been performed accurately and the chemicals and distilled water are of the specified purity, the absorbing reagent will have a pH of approximately 4.0. The reagent is acceptable for use if the pH is between 3 and 5. However, a significant deviation from a pH of 4.0 (e.g., pH < 3.5 or > 4.5) although acceptable, would tend to indicate poor laboratory procedure or impure chemicals and should serve as a warning to exercise more care in preparing the next batch. In the event that the pH is outside the 3 to 5 range, discard the reagent and check the chemicals and procedure before preparing another batch.

Collection efficiency check - As a check on the collection efficiency of a new batch of absorbing reagent, it is suggested that dual samples be collected and analyzed using two absorbers, one filled with absorbing reagent from the old batch and the other filled with the new reagent.

Compute the difference in the two measured concentrations by

$$d = (\mu g\ SO_2/m^3)_n - (\mu g\ SO_2/m^3)_o$$

where d = the difference in $\mu g\ SO_2/m^3$,

$(\mu g\ SO_2/m^3)_n$ = SO_2 concentration measured with new reagent,

and $(\mu g\ SO_2/m^3)_o$ = SO_2 concentration measured with old reagent.

If d is less than or equal to $[44 + .063\ (\mu g\ SO_2/m^3)_o]\ \mu g\ SO_2/m^3$, the new reagent is accepted as no different than the old reagent (at the 3σ level). If d is greater than the above value and there is no reason to suspect the old absorbing reagent of having deteriorated, or an analysis error, the new batch should be discarded and additional absorbing reagent prepared.

If a calibrated SO_2 permeation tube is used for developing a calibration curve (see Subsection 8.2.2 of the Appendix), the results include the correction for collection efficiency and the above check need not be made.

Storage of absorbing reagent - Absorbing reagent can be stored in a stoppered container. It is normally stable for 6 months. It should be checked visually before each use and discarded if a precipitate has formed.

Flow Rate Calibration (Step 2)

Flow rates in the range of about 900 to 1100 cm^3/min, 450 to 550 cm^3/min, and 180-220 cm^3/min are used for 30-minute, 1-hour, and 24-hour sampling periods, respectively. It is recommended that rotameters or critical orifices used for the 30-minute and 1-hour sampling periods be calibrated against a wet test meter or a soap-bubble meter. Flowmeters used for 24-hour sampling should be calibrated against a soap-bubble meter for best results.

It should be noted that the above flow rate ranges are only approximate. However, as long as these ranges are observed the flow rate will not be so great as to (1) result in entrainment of the absorbing reagent, (2) cause excessive evaporation of the absorbing reagent (e.g., more than 10 to 20 percent of the total quantity), or (3) collect large quantities of SO_2 necessitating the dilution of samples before analysis. The lower limit will in general result in a sample volume of air large enough to ensure the collection of a quantity of SO_2 in the analytical range.

Rotameters should be removed from the system and cleaned every six months, or after 30 days of operation, whichever occurs first. It is recommended that rotameters be calibrated after being cleaned, at any signs of erratic behavior, or any time the flow rate measured by the rotameter differs by

as much as 4 percent from the flow rate measured by a calibrated flowmeter. Calibrated rotameter as used here refers to a rotameter that has been calibrated against a wet test meter or a soap-bubble meter.

Critical orifices are calibrated before and after each sampling period.

Rotameter Calibration - A rotameter is calibrated within an apparatus similar to the field sampling collection device. The absorber assembly should conform to the same specifications as the field collection device, and contain a volume of distilled water or absorbing reagent equal to the volume of absorbing reagent used in the field device.

Calibration of a rotameter against a wet test meter - Figure 2 shows a typical setup for calibrating a rotameter against a wet test meter. The calibration procedure is as follows:

(1) Set up the apparatus as shown in Figure 2 making the connections as short as possible and of the same inside diameter as is used in the field sampling train.

(2) Start the air flowing through the system and allow to flow for 5 to 10 minutes to allow the water in the wet test meter to reach saturation with the air.

(3) Before and after the complete calibration run, read and record room temperature and barometric pressure. Record average values on the calibration form in Figure 3. Use average values for subsequent calculations.

(4) Adjust the flow rate to about 20 percent of full scale for the rotameter with the needle valve.

(5) Take a pair of timed readings on the wet test meter (for best results use complete revolutions of the wet test meter), under steady flow, for each of five or more uniformly spaced points on the rotameter scale, going from low values to high values. Repeat, going from high to low. Record rotameter reading, total flow, elapsed time of run, manometer reading at the wet test meter, manometer reading at the rotamter, and T_m (temperature of the liquid in the wet test meter) for each run on the calibration sheet of Figure 3.

(6) Convert all temperature and pressure readings to absolute units.

$$°C + 273 = °K$$

$$\text{in } H_2O \times 1.87 = \text{mmHg}.$$

(7) For each run correct the volume measured by the wet test meter to the volume measured by the rotameter by

$$V_r = \left(\frac{T_r}{T_m}\right)\left(\frac{P_m}{P_r}\right)(V_m)$$

where V_r = volume of air passing through the rotameter at T_r and P_r,

T_r = temperature of air entering rotameter (taken as the temperature of the liquid in the absorber),

P_r = barometric pressure minus the reading of the manometer just upstream of the rotameter.

V_m = volume measured by the wet test meter,

P_m = barometric pressure plus the reading of the manometer on the wet test meter,

and T_m = temperature of the liquid in the wet test meter.

(8) For each V_r calculate the corresponding flow rate by dividing the corrected volume, V_r, by the elapsed time, t, in minutes for that run as

$$Q_r = V_r/t \ .$$

(9) For each run use a general form of the rotameter equation to calculate

$$K = \left(Q_r/I\right)\left(\frac{P_r}{T_r}\right)^{1/2}$$

where I = rotameter reading (considered dimensionless here)

Q_r = flow rate from procedure 8 above (cm^3/min),

P_r = pressure at rotameter (barometric pressure minus manometer reading)(mmHg),

T_r = temperature of air at rotameter (°K), and

K = determinable rotameter equation constant with appropriate units to make the equation dimensionally consistent.

(10) Plot on Cartesian Coordinates K (y-axis) versus I (x-axis) for all runs. Use regression analysis or by eye construct a best-fit curve to the data points. The curve should approximate a straight line with zero slope. Figure 4 is a hypothetical rotameter calibration curve. Mark the values of T_r and P_r on the graph.

(11) Check all plotted points and rerun any that deviates more than $\pm$ 5 percent from the best-fit curve for a fixed rotameter indication. Compute the percent deviation by

$$\text{percent deviation} = \frac{K_1 - K_2}{K_2} \times 100$$

where K_1 = the K value of the plotted point, and

K_2 = the K value read from the best-fit curve for the same rotameter reading as for K_1.

(13) Forward calibration curve and data to supervisor for his approval. File the approved data and curve in the calibration log book.

Calibrating a rotameter against a soap-bubble meter - Calibrating a rotameter against a soap-bubble meter can be accomplished with the same type apparatus setup as shown in Figure 2 with a soap-bubble meter replacing the wet test meter. The calibration procedure is as follows:

(1) Connect the apparatus as shown in Figure 2 with the soap-bubble meter replacing the wet test meter. Use apparatus having the same specifications as the actual sampling train.

(2) Either immediately before or after the calibration, measure and record on the calibration form in Figure 3 the ambient temperature and barometric pressure.

(3) Adjust the flow rate to about 20 percent of full scale for the rotameter with the needle valve.

(4) Take a pair of timed readings on the soap-bubble meter under steady flow, for each of five or more uniformly spaced points on the rotameter scale, going from low values to high values. Repeat, going from high to low. Record rotameter reading, manometer reading at rotameter, total flow and elapsed time for each run on the calibration sheet of Figure 3.

Note: In Figure 3 the column for manometer for the wet test meter reading is not used when calibrating against a soap-bubble meter; also, T_m becomes the same as room temperature.

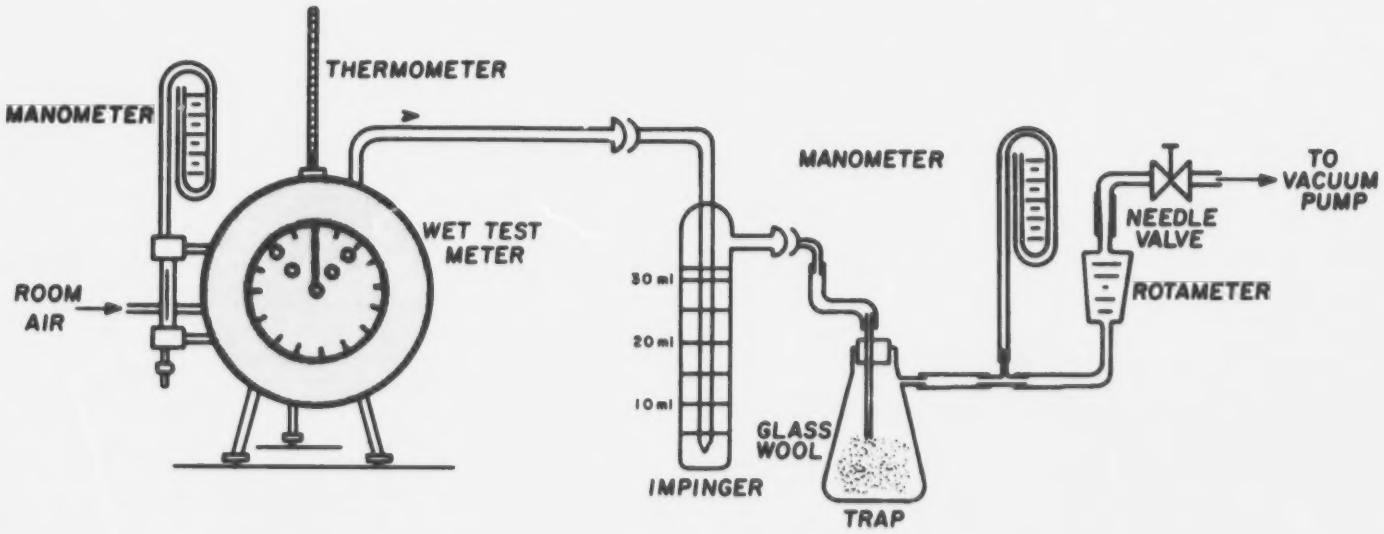

Figure 2: Schematic of Setup for Calibrating a Rotameter Against a Wet Test Meter

ROTAMETER SERIAL NO._____ CALIBRATED WITH_____

LOCATION_____ AMBIENT/ROOM TEMPERATURE (Average)_____°K

ATMOSPHERIC PRESSURE (Average)_____ RELATIvE HUMIDITY_____

CALIBRATED BY_____ DATE_____

Test Point	Rotameter Reading	Total Flow	Elapsed Time	Manometer Reading		$V_r=\left(\frac{T_r}{T_m}\right)\left(\frac{P_m}{P_r}\right)V_m$	$Q_r = V_r/t$	$K=(Q_r/I)(P_r/T_r)^{1/2}$
				Wet Test Meter	Rotameter			
1								
2								
3								
4								
5								
6								
7								
8								
9								
10								

Figure 3: Rotameter Calibration Data Sheet

FLOWMETER NO._____ TEMPERATURE AT CALIBRATION (°K)_____

LOCATION_____ ATMOSPHERIC PRESSURE AT CALIBRATION (mmHg)____

CALIBRATED BY_____

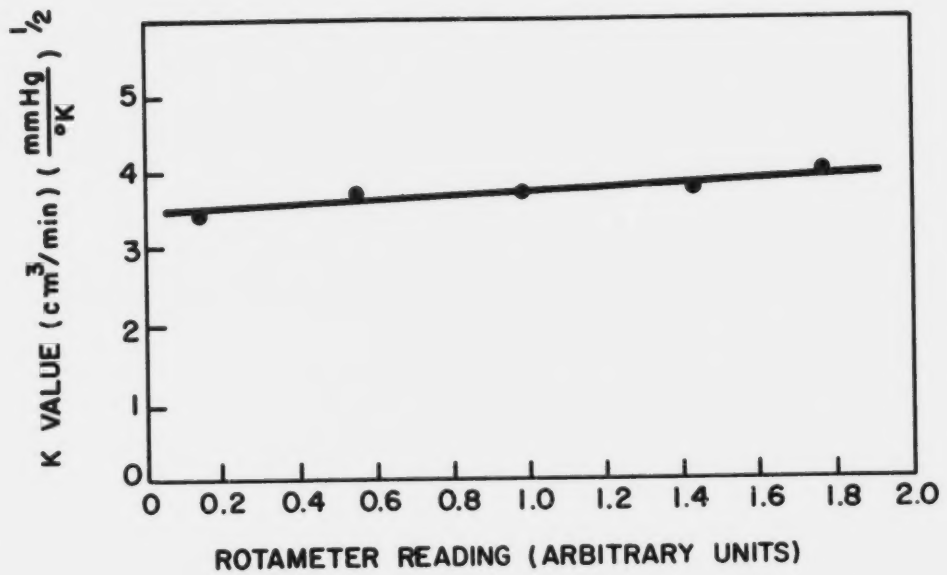

Figure 4: Hypothetical Rotameter Calibration Curve

(5) Convert all temperature and pressure readings to absolute units.

$$°C + 273 = °K$$

$$\text{in } H_2O \times 1.87 = \text{mmHg}.$$

(6) For each run, correct the flow rate measured by the soap-bubble meter to the flow rate measured by the rotameter by

$$Q_r = \left(\frac{T_r}{T_m}\right)\left(\frac{P_m}{P_r}\right)(Q_m)$$

where Q_r = flow rate through the rotameter at T_r and P_r, cm^3/min.

T_r = temperature of air entering rotameter (taken as the temperature of the liquid in the absorber), °K.

P_r = barometric pressure minus the reading of the manometer just upstream of the rotameter, mmHg,

Q_m = flow rate measured by the soap-bubble meter, cm^3/min,

P_m = barometric pressure, mmHg,

and T_m = room temperature, °K.

(7) For each run use a general form of the rotameter equation to calculate

$$K = (Q_r/I)\left(\frac{P_r}{T_r}\right)^{1/2}$$

where I = rotameter reading (considered dimensionless here),

Q_r = flow rate from procedure 6 above (cm^3/min),

P_r = pressure at rotameter (mmHg),

T_r = temperature at rotameter (°K),

and K = determinable rotameter equation constant with appropriate units to make the equation dimensionally consistent.

(8) Plot on Cartesian coordinates K (y-axis) versus I (x-axis) for all runs. Use regression analysis or by eye construct a best-fit curve to the data points. The curve should approximate a straight line with zero slope. Figure 4 is a hypothetical rotameter calibration curve.

(9) Check all plotted points and rerun any that deviates more than $\pm$ 5 percent from the best-fit curve for a fixed rotameter indication. Compute the percent deviation by

$$\text{percent deviation} = \frac{K_1 - K_2}{K_2} \times 100$$

where K_1 = the K value of the plotted point,

and K_2 = the K value read from the best-fit curve for the same rotameter reading as for K_1.

(10) Forward calibration curve and data to supervisor for his approval. File the approved data and curve in the calibration log book.

Calibration of Critical Orifice - A critical orifice is calibrated within an apparatus similar to the sampling train used in the field. That is, the absorber assembly and tubing should conform to the same specifications as the ones used when sampling. It is recommended that either a soap-bubble meter or a calibrated rotameter be used to calibrate critical orifices for 24-hour sampling where the flow rate is around 200 cm^3/min. A wet test meter, soap-bubble meter, or calibrated rotameter can be used for calibrating the orifices for 30-minute and 1-hour sampling.

The calibration procedure is written in terms of a wet test meter with special notes when the procedure would be different if a soap-bubble meter or rotameter were used. The procedure is as follows:

(1) Connect the apparatus as shown in Figure 5.

(2) Turn the vacuum pump ON and check the sampling train for leaks by slightly adjusting each connection while watching the manometer (the one next to the critical orifice) for any fluctuation in pressure. Experience will indicate approximate pressure drops for the different sampling trains. Too small a pressure drop indicates leaks in the system and too high pressure drops indicates a restriction in the sample lines.

Eliminate all leaks or restrictions before continuing.

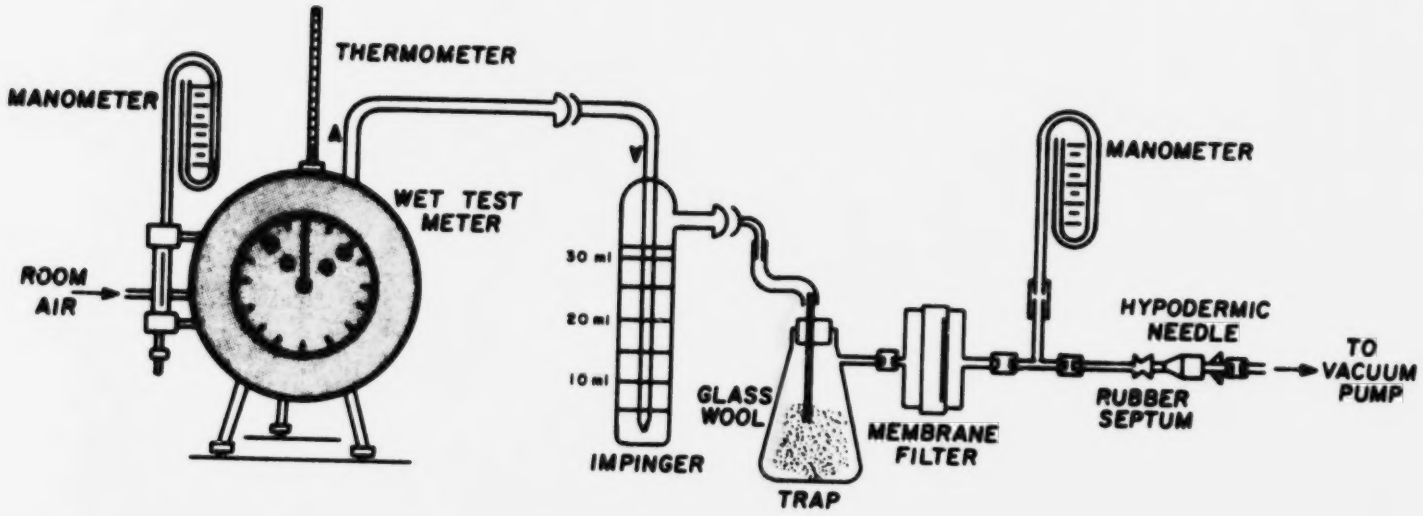

Figure 5: Schematic of Setup for Calibrating a Critical Orifice Against a Wet Test Meter

(3) To assure that the orifice is critical, read the vacuum gauge on the vacuum pump (see Figure 7; the vacuum gauge is mounted on top of the pump and connected to the pump's inlet port) and compare that reading to the pressure immediately upstream of the critical orifice. This upstream pressure is obtained by subtracting the reading of the manometer directly upstream of the critical orifice from barometric pressure. The orifice is critical if

$$P_v \geq 0.55\ P_u$$

where P_v = reading of vacuum gauge (mmHg),

and P_u = barometric pressure minus manometer reading (mmHg).

See Reference 1 for a more detailed discussion of critical flow.

For the 24-hour sampling train the upstream pressure is usually on the order of 735 mmHg (~29 in Hg) therefore, the vacuum gauge reading must be greater than 405 mmHg (> 16 in Hg) for the orifice to be critical. Normal practice is to use a pump that will maintain a vacuum greater than 507 mmHg (20 in Hg).

If sufficient vacuum cannot be obtained, the system probably has leaks or the vacuum pump needs replacing.

(4) Measure and record on the calibration record sheet; (1) ambient/room temperature, (2) barometric pressure, and (3) relative humidity.

(5) A. Make at least three timed runs when using a wet test meter. Time at least one complete revolution of the wet test meter per run.

Record the total flow (volume) measured by the wet test meter, elapsed time of run, and both manometer readings for each run.

B. If a soap-bubble meter is used, make at least three timed runs. Record the elapsed time, and the manometer (for the critical orifice) reading for each run.

C. When using a calibrated rotameter make three readings by shutting the pump OFF momentarily between readings. Record the rotameter reading and the manometer (for the critical orifice) reading for each run.

(6) Correct the indicated volume/flow rate to the temperature and pressure at the orifice by:

A. For a wet test meter use

$$V_r = \left(\frac{T_r}{T_m}\right)\left(\frac{P_m}{P_r}\right)(V_m)$$

for each of the three runs;

where V_r = volume of air passing through the critical orifice at T_r and P_r, cm^3,

T_r = temperature of air entering the orifice (taken as the temperature of the liquid in the absorber which should be room temperature), °K,

P_r = barometric pressure minus the reading of the manometer just upstream of the orifice, mmHg,

V_m = volume of air measured by the wet test meter, cm^3,

P_m = barometric pressure plus the reading of the manometer on the wet test meter,

and T_m = temperature of the liquid in the wet test meter, °K.

Note: Under this setup the difference in V_r and V_m should be fairly small since $T_r \simeq T_m$ and P_r differs from P_m by about 25 mmHg or less.

Compute the critical volumetric flow rate of the orifice at T_r and P_r for each of the runs by

$$Q_r = V_r/t$$

where t = the elapsed time of the run in minutes.

Compute the average, $\bar{Q}_r$, from the three runs and use this value in subsequent calculations.

B. When using a soap-bubble meter convert the measured volumetric flow-rate to the volumetric flow rate at the orifice for all three runs by

$$Q_r = \left(\frac{T_r}{T_m}\right)\left(\frac{P_m}{P_r}\right)(Q_m)$$

where Q_r = flow rate as would be measured by the soap-bubble meter at orifice conditions of T_r and P_r, cm^3/min,

T_r = temperature of air upstream of the orifice (taken as temperature of the absorbing reagent which should be room temperature, °K,

P_r = barometric pressure minus reading of the manometer upstream from orifice, mmHg,

Q_m = flow rate measured by soap-bubble meter, cm^3/min,

P_m = barometric pressure, mmHg,

and T_m = room temperature, °K.

Note: The difference in Q_r and Q_m should be fairly small when using the setup of Figure 5 since $T_r \simeq T_m$ and P_r differs from P_m by approximately 25 mmHg.

C. When a rotameter is used as the standard, it should itself be calibrated against a high grade soap-bubble meter as discussed in Step (2), starting on page 10. Proceed as follows:

(1) Average the three rotameter readings to get $\bar{I}$. From the calibration curve for the rotameter determine the value of K corresponding to a rotameter reading of $\bar{I}$.

(2) Compute the measured flow rate by

$$Q_m = K\bar{I}\left(\frac{T_m}{P_m}\right)^{1/2}$$

(3) Convert the measured flow rate to the flow rate at orifice conditions of T_r and P_r by

$$Q_r = \left[\frac{T_r}{T_m}\frac{P_m}{P_r}\right]^{1/2} Q_m$$

where Q_r = flow rate at the orifice conditions of T_r and P_r, cm^3/min,

T_r = temperature of air upstream of orifice (taken of absorbing reagent or room temperature), °K,

P_r = barometric pressure minus reading of the manometer upstream of critical orifice, mmHg,

Q_m = flow rate measured by rotameter at conditions T_m and P_m, cm^3/min,

T_m = ambient room temperature, °K,

and P_m = barometric pressure, mmHg.

(7) Once Q_r has been determined by either of the above three methods, calculate

$$K = Q_r/(T_r)^{1/2}$$

(8) Record the K value and date of calibration in the calibration log book for that critical orifice.

A critical orifice should be discarded at any time its original K value cannot be duplicated to within $\pm$ 2 percent after having been cleaned.

Absorber Preparation (Step 3)

Selection of Absorbers - Select absorbers appropriate for the sampling period to be used according to the specifications given in Section 5 of the Appendix, page 113.

Cleaning Absorber Assembly - Before each use it is recommended that the absorber assembly be cleaned by washing with hot water and placed in an acid bath consisting of 1 part nitric acid, 2 parts hydrochloric acid, and 4 parts distilled water for 1 hour. Then rinse thoroughly with distilled water and allow to dry.

Dispensing of TCM (Absorbing Solution) Into Absorbers - Transfer quantities of TCM, appropriate for the sampling period to be used, as specified in Section 7 of the Appendix into the absorber.

Note: If the situation requires shipping apparatus from the central laboratory to the field site and vice versa, it is recommended that for 30-minute and 1-hour samples and all-glass midget impinger remain on site and the TCM be shipped in test tubes with screw-on caps using a teflon or equivalent inner liner on the caps. The TCM would then be quantitatively transferred to the impinger by the field operator.

For 24-hour sampling the use of a set-volume reagent dispenser, such as a 50 mℓ repipet, for dispensing absorbing reagent into the absorbers is fast and reduces the chance of a volume error.

Assemble the absorber as shown in the drawing of Figure 6. Two tubing caps are fitted on the tube ends to guard against contaminating the absorbing reagent. Shrinkable tape can be used around the tube and closure to add mechanical stability and discourage tampering. Alternatively, a threaded absorber tube and screw-on cap could be used. To guard against accidentally forcing absorbing reagent out of the absorber, it is important to always install the tube cap on the impinger tube first. Color coding the tube cap and tube would aid field personnel in identifying the cap and act as a reminder to install that cap first.

On the first filling and after assembly, the absorber should be scribed or otherwise permanently marked at the 50 mℓ level. Glass impingers for 30-minute and 1-hour sampling come from the factory with a permanent scale.

Sample Identification (Step 4)

Each absorber should have the following identifying information semi-permanently affixed by a stick-on label or marked directly on the absorber with a felt-tipped pen:

(1) date absorber was prepared,

(2) sampling site number, and

(3) date to be used.

Obtain a calibrated critical orifice, if used in the system, and attach to the absorber (see Step 5 below). Record the absorber identifying information, orifice number and date to be shipped in the laboratory log book.

Package for Shipment (Step 5)

In situations where shipping by mail is required, a container like or equivalent to that used by EPA in the NASN program should be used. The container is a block of wood with drilled holes of the proper sizes for holding the absorbers and critical orifices. This type container remains serviceable for a long period of time.

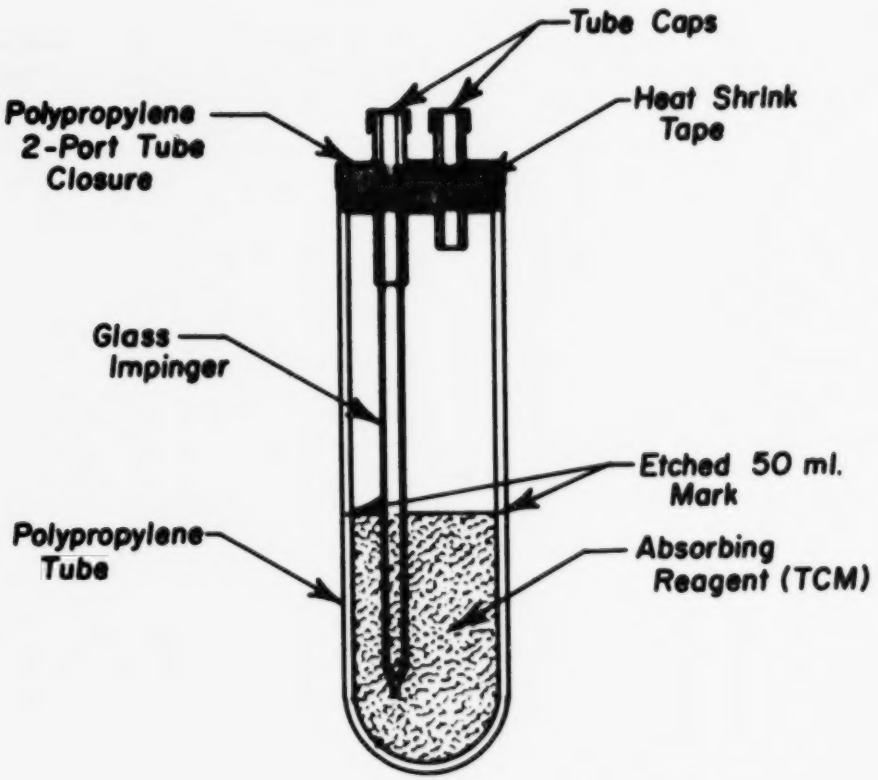

Figure 6: An Absorber (24-Hr Sample) Filled and Assembled For Shipment

SAMPLE COLLECTION

Sampling Apparatus Assembly (Step 6)

A typical sampling system consists of a collection unit, vacuum pump, and a 7-day timer as shown in Figure 7. The collection unit, in this case, is a metal box which houses the sampling train. The sampling train is maintained at a near constant temperature with a thermostatically controlled heater.

Sampler Assembly - General guidelines are given for assembling a sampling system used by EPA in the NASN program as shown in Figure 7. Assemble as follows:

(1) Attach the membrane sample air filter unit to the glass inlet manifold. The connecting tubing passes through a cutaway in the sampler box. Support for the filter is provided by the tubing resting on the cutaway. Care should be exercised when installing or changing the filter so as not to break the glass manifold. Figure 8 is a picture of a sampling train with the filter installed.

(2) Attach the sample inlet line consisting of polypropylene tubing and funnel to the sample air filter as shown in Figure 7. Extend the funnel and sample inlet line out-of-doors through a window or other opening. Support and secure the tube and funnel in position so that they will not come loose during sampling. The funnel should be positioned to hang down so that rain will not be drawn into the sampler.

(3) Connect the metal exhaust manifold to the intake of the vacuum pump with tygon tubing. Place a pinch clamp on this section of tubing as shown in Figure 9, but do not tighten. Be sure all connections are airtight and that there are no constrictions in the tubing.

(4) Electrically connect the vacuum pump to the timer (see Figure 7) and the timer to a 24-hour 110 VAC outlet. The sampler box is also connected to a 24-hour outlet.

Installation of Absorber and Critical Orifice - Correct installation of the reagent-filled absorber and calibrated orifice is vital to the collection of a valid sample. Color-coding schemes for the absorbers and tubing are frequently used to assist in locating absorbers in the right positions and for making correct connections. One such scheme is used in the following procedure. A close-up view of the absorber installation is given in

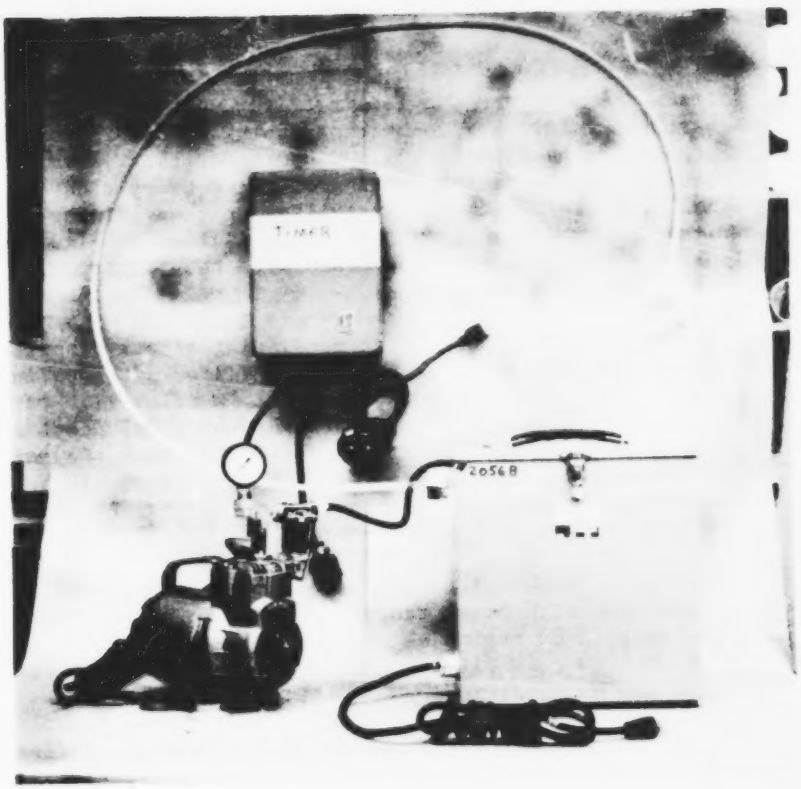

Figure 7: Sampling Apparatus Assembly

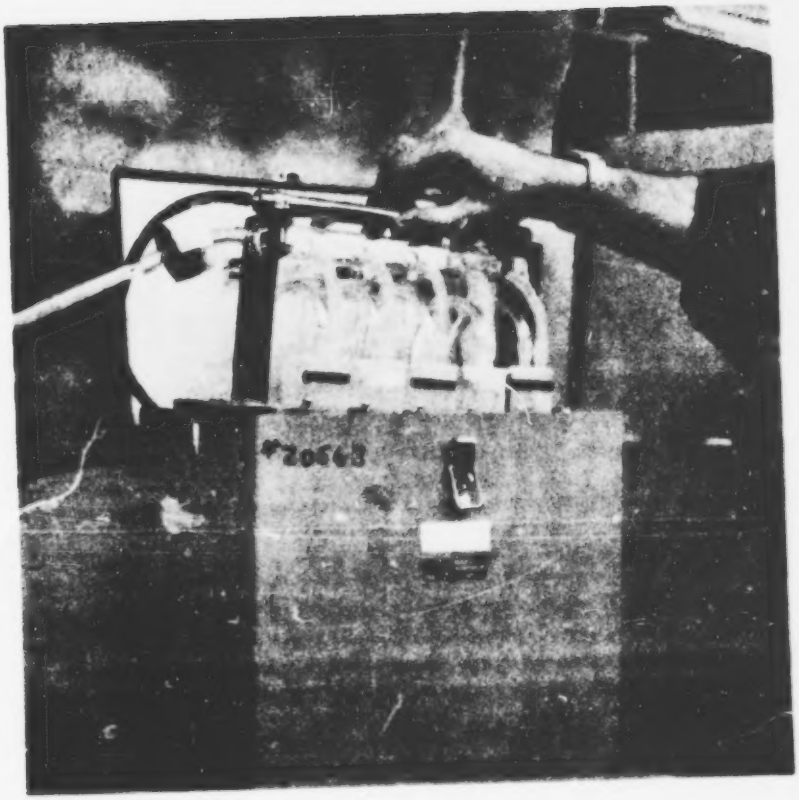

Figure 8: Sampling Train With Sample Air Filter Installed

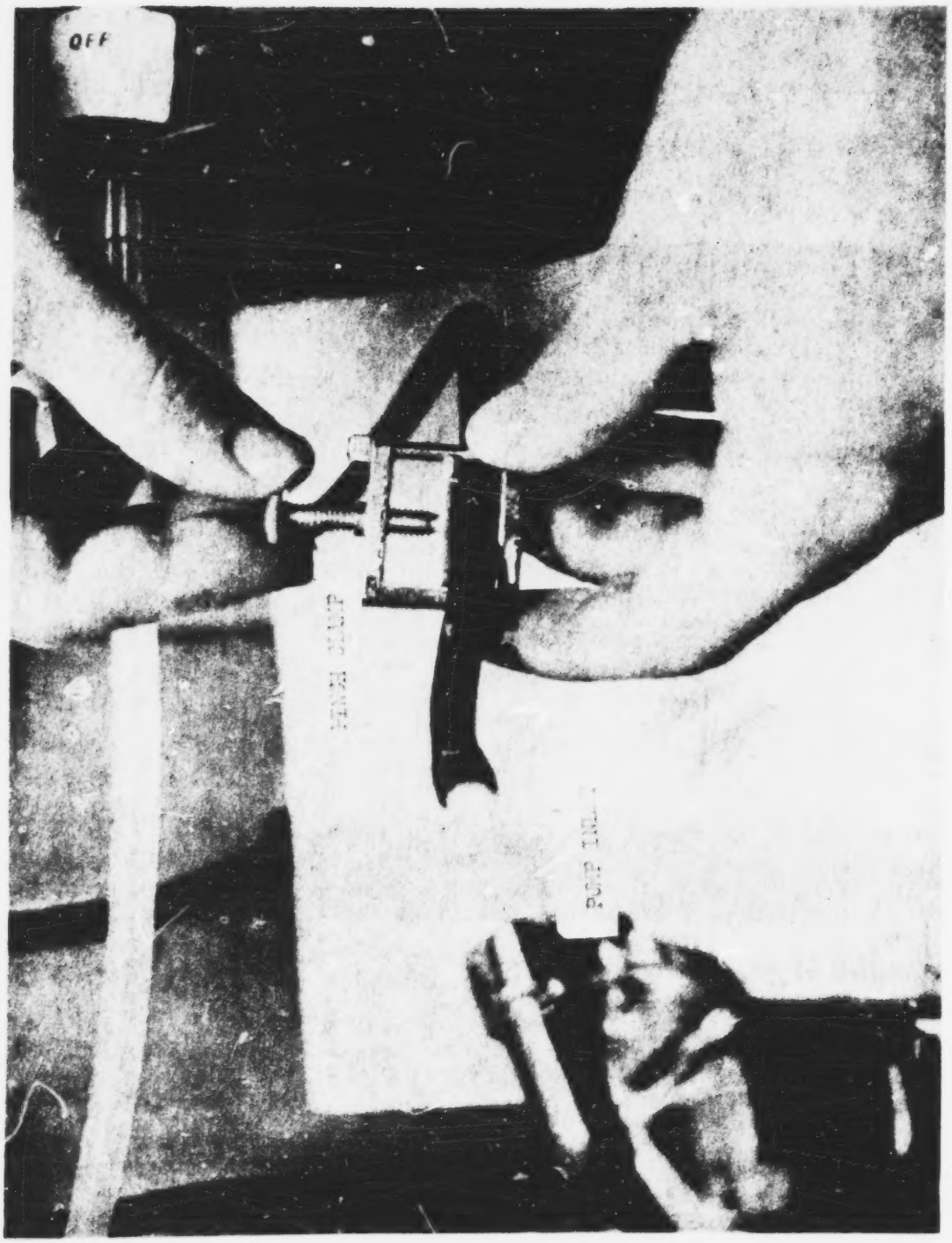

Figure 9: Installation of Pinch Clamp on Vacuum Pump Inlet Line

Figure 10. In this setup the top of the absorber around the impinger tube and the tube cap on the impinger tube are color-coded. An accordian type of tubing is used to connect the glass intake manifold to the impinger tube. Smooth tubing is used for all other connections.

The installation procedure is as follows:

(1) Remove the dummy absorber (or used absorber) from the sampling train by gently but firmly pulling the inlet and outlet tubing from the absorber as shown in Figure 11.

(2) Exchange the reagent-filled absorber for the dummy absorber.

(3) Transfer the caps from the reagent-filled absorber to the dummy absorber. Caution: Always install the tube cap or tubing on the impinger tube (color-coded side of absorber) first and remove them last, otherwise some of the absorbing reagent/sample may be forced out the impinger opening and be lost.

(4) Gently but firmly insert the accordian inlet tube (from the glass manifold) onto the color-coded tube (impinger tube) of the absorber lid. Make certain the fit is airtight.

(5) Gently but firmly insert the smooth tubing (from the trap) to the unpainted outlet tube of the absorber.

(6) Remove the critical orifice (calibrated hypodermic needle) from the shipping container. Note: It is important that the needle be used and returned with the absorber that it was received with.

For systems using a calibrated rotameter to measure flow-rate the rotameter remains in the sampling train until it is removed for cleaning and calibration.

(7) Insert the new needle into the center of the rubber stopper attached to the membrane filter unit as shown in Figure 12. The needle must be put in straight. If the needle is accidently bent during installation, it should be discarded and another absorber and needle used.

(8) Slide the base of the needle onto the metal exhaust manifold as shown in Figure 13. Manipulate the needle and/or rotate the trap, if necessary, to obtain a tight connection.

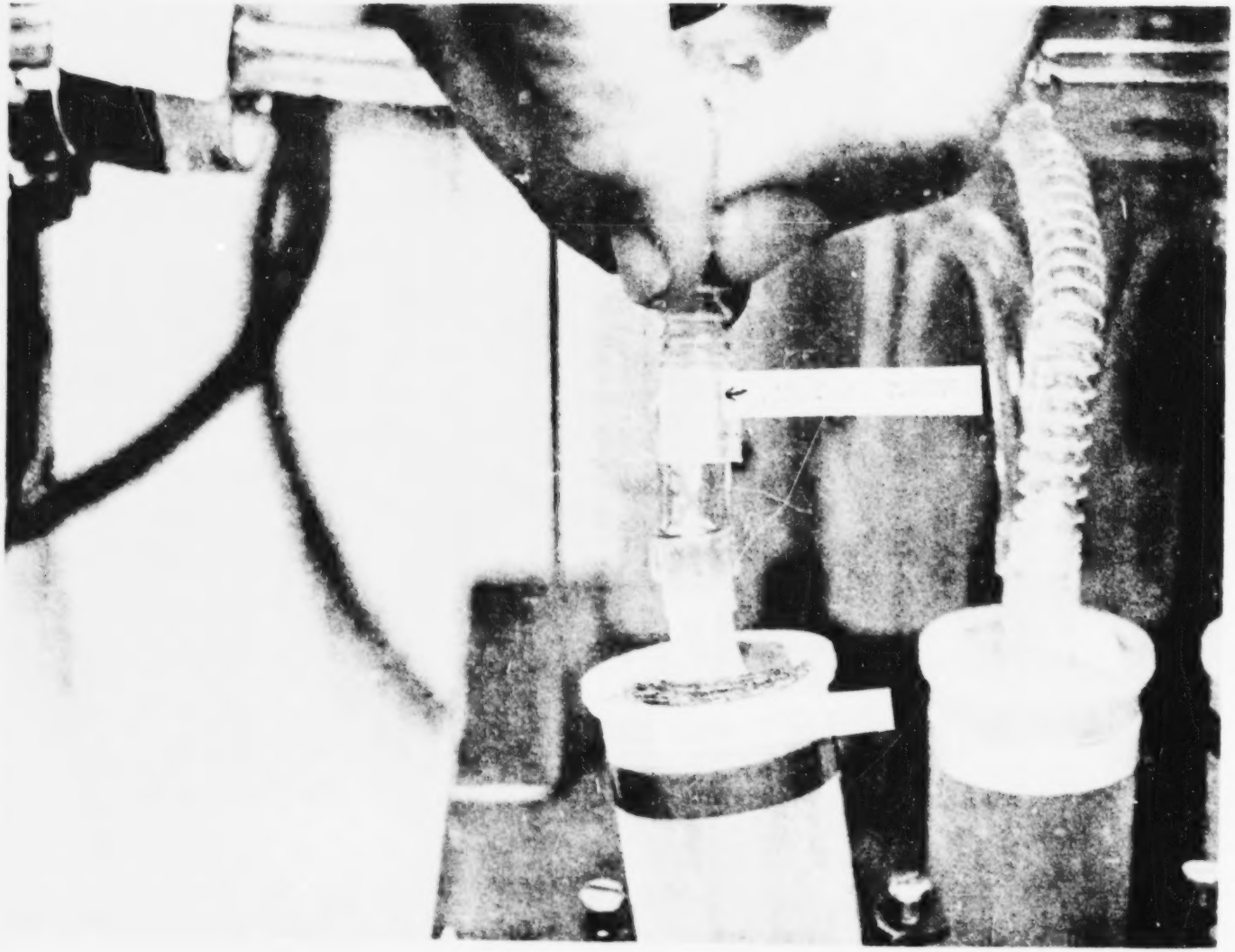

Figure 10: Close-up View of Absorber Installation

Figure 11: Removal of Dummy Absorber From Sampling Train

Figure 12: Installation of Critical Orifice in the Sampling Train

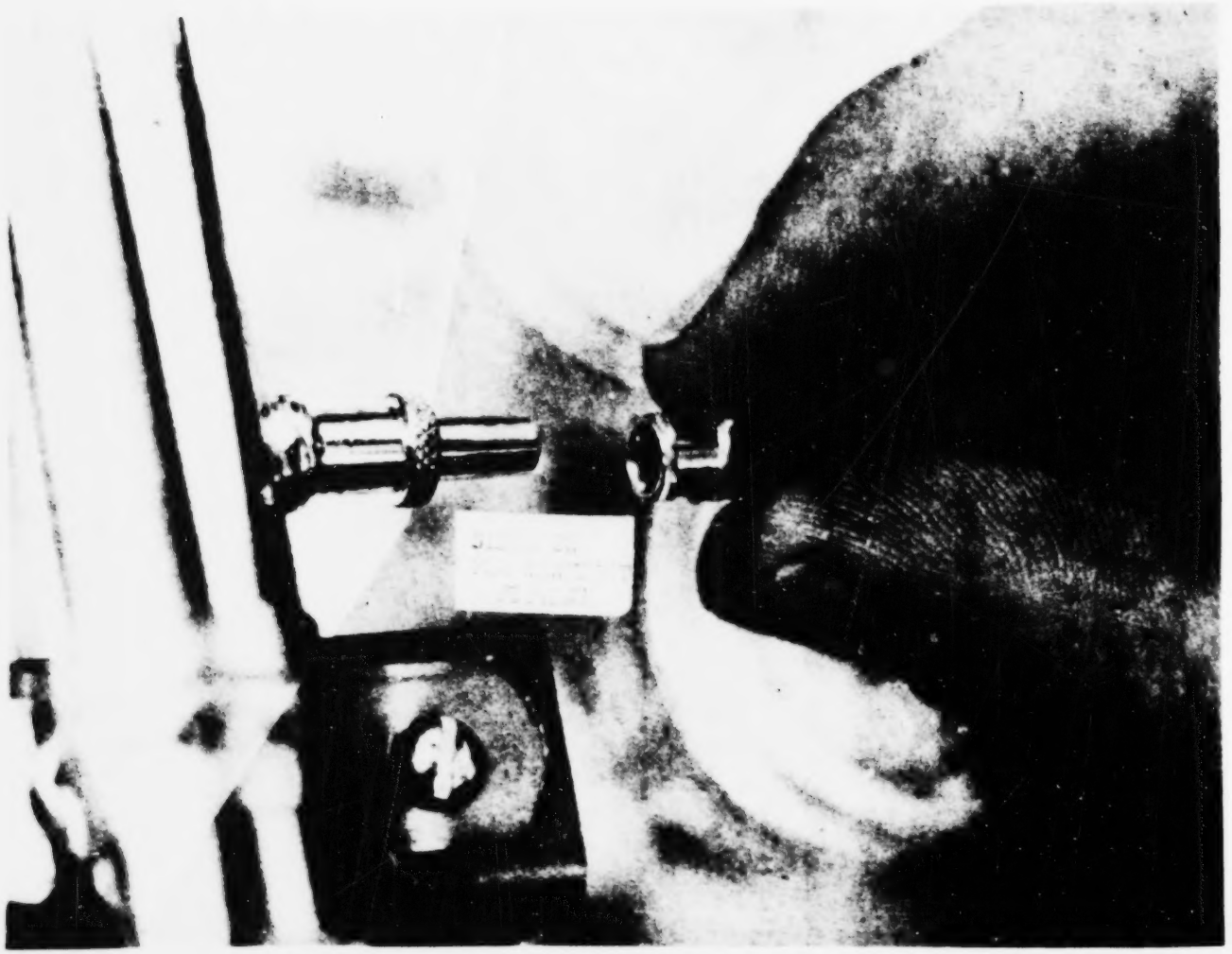

Figure 13: Connecting Critical Orifice to Exhaust Manifold

(9) Recheck the arrangement, alignment, and tightness of all connections. The following points should be verified:

(a) The accordian tubing from the glass manifold goes to the color-coded side of the absorber lid;

(b) the needle is not bent or obstructed;

(c) the needle forms a tight fit at the exhaust manifold;

(d) the inlet filter and tubing is tightly connected, and

(e) the vacuum pump connections are tight.

Note: In situations where the sampling train is not housed in a closed box the absorber must be shielded from sunlight during and after sampling. One means of accomplishing this is to wrap the absorber in aluminum foil.

Operational Check of System (Step 7)

(1) If a critical orifice is used in the system completely close the pinch clamp between the sampler and the vacuum pump (see Figure 9).

(2) Turn the timer switch to the ON position. This should start the vacuum pump.

(3) For systems using a critical orifice, record the vacuum gauge reading to the nearest whole number on the Sample Record Sheet of Figure 14, in the space marked "Start-Clamp." The gauge should read above 508 mmHg (20 in Hg) vacuum. If it does not, make sure the pinch clamp is closed and the tubing is securely connected to the pump inlet. If the vacuum reading remains below 508 mmHg (20 in Hg) the pump should be replaced. Continue to (4) below.

If a rotameter is used check and if necessary adjust the system flow rate to the prescribed value (e.g., 200 cm^3/min (.2 ℓ/min) for a 24-hour sample) and record the value on the Sample Record Sheet under "Remarks." Continue with (5) below.

(4) Open the pinch clamp. Record the vacuum gauge reading on the Sample Record Sheet in the space marked "Start-Open." The gauge should read a little less than the reading with the clamp closed. If it reads below 508 mmHg (20 in Hg), check for a loose connection at the pump.

SAMPLER SERIAL NUMBER_____ SHIPPING PACKAGE NUMBER_____

SITE IDENTIFICATION: CITY OR TOWN _____, STATE_____, SAMPLER LOCATION_____

WIND	VISIBILITY	HUMIDITY	AVERAGE TEMP (°C)	AVERAGE PRESSURE (mmHg)
_____ DIRECTION [ ] CALM [ ] LIGHT [ ] GUSTY	[ ] CLEAR [ ] HAZY	[ ] CLEAR [ ] SCATTERED [ ] OVERCAST		

DATE_____	METER READING			REMARKS & UNUSUAL CONDITIONS OR ACTIVITIES NEAR THE SITE
		OPEN	CLAMP	
[ ] 0000 TO 2400 HOURS	START			
[ ] OTHER EXPLAIN	END			

Figure 14: Sample Record Sheet

(5) Record on the Sample Record Sheet the date that the sample was collected (one day only), and the time (if other than 0000-2400 explain under "Remarks").

(6) Gently lift the sampling train halfway out of the sampler box (do not tilt the train) as in Figure 8. Examine the absorber to make certain that it is bubbling. If not, check for loose connections or a plugged line in the train and correct.

(7) Turn the timer OFF and set for sampling period.

Sample Collection (Step 8)

The sampling period is started and stopped by the timer. The absorbing reagent should be protected from direct sunlight during and after sampling by covering the absorber with aluminum foil if it is to remain outside the sampler or shipping block for any period of time. At the end of the sampling period, perform the following operations:

(1) With the timer switch ON, record the vacuum gauge reading on the Sample Record Sheet in the space marked "End-Open" if a critical orifice is being used and continue to (2) below. For systems using a rotameter read and record the final flow rate, turn the timer switch to OFF, and continue with (4) below.

(2) Close the pinch clamp as tight as possible. Record the vacuum gauge reading on the Sample Record Sheet in the space marked "End-Clamp."

(3) Turn the timer switch to the OFF position. Open the pinch clamp.

(4) Check the condition of the membrane filter. Replace if it is discolored or cracked.

(5) If the ambient temperature is below the thermostat setting in the sampling box, check to see that the thermostat and heater are working.

(6) If possible, obtain an average temperature of the absorbing reagent for the sampling period. For 30-minute and 1-hour sampling periods a temperature reading immediately before, after or any time during the period could be used as an average for the sampling period.

For 24-hour sampling periods two approaches are discussed for arriving at an estimate of the average temperature.

(a) Place a minimum maximum thermometer in the thermostated box used to house the sampling train. Report the average of the minimum and maximum temperatures for that sampling period. The thermometer has to be reset before each sampling period.

(b) If a thermometer is not available for (a) above, the average temperature can be reported as the normal thermostatic setting of the box or ambient temperature, whichever is greater.

(7) Determine and report the barometric pressure by maintaining a barometer on-site, or in the near vicinity. Read and report the barometric pressure each sampling period. Alternatively, the pressure can be obtained from the nearest weather station provided the altitudes of the weather station and sampling site do not differ by more than about 61 m (~200 ft).

The barometric pressure seldom varies more than 2 or 3 percent from a mean value for a given site. Therefore, unless a high degree of accuracy is required, an average pressure derived from 20 to 30 days of data can be used as the barometric pressure for that site. Also, barometric pressure is not required when a critical orifice is used to control the flow rate.

Sampling Handling (Step 9)

(1) Remove the exposed absorber from the sampling train. Remove the accordian tubing (from the galss manifold) from the absorber first. Check the absorber and if any of the reagent has evaporated, use fresh absorbing reagent to bring it up to the 50 mℓ mark (24-hour sample). Record on the Sample Record Sheet the quantity of absorbing reagent (mℓ) or state under "Remarks" that there was no evaporation. If the absorber is estimated to have less than 35 mℓ the sample should be invalidated by so stating on the record sheet. The absorber and record sheet should be forwarded to the supervisor. If there are signs that indicate that part of the absorbing reagent was forced out of the absorber into the system, absorbing reagent should not be added and the situation noted on the Sample Record Sheet.

(2) Replace the tube caps on the exposed absorber. Be sure to place the cap over the impinger tube opening near the painted side of the absorber lid first. Press both caps on firmly and place the absorber in the shipping block. Note: where glass impingers are used replace any evaporated absorbing reagent, shake thoroughly, then transfer the exposed reagent to a test tube with a teflon-lined, threaded cap. Place the test tube in the shipping block.

(3) If a critical orifice was used, disconnect the base end of the hypodermic needle from the metal exhaust manifold and remove the needle from the rubber stopper and place the needle in the shipping block with the exposed absorber. Note: The needles must be returned with the absorber that it was used with.

(4) Record on the Sample Record Sheet any unusual activities or conditions near the site such as fires involving burning coal or oil, large coal burning power plants, smoking stacks, rain, snow, fog, inversions, or other conditions that may affect the pollution level.

(5) Fill out the Sample Record Sheet in duplicate. Fold the original copy and wrap around the absorber in the shipping block. File the duplicate copy in the site log book.

(6) Deliver the sample to the laboratory or pack the absorber (and critical orifice) in a mailing container, affix the return mailing label, and mail promptly.

SAMPLE ANALYSIS

Verify Documentation (Step 10)

Check the Sample Record Sheet for any missing information that would invalidate the sample. If sufficient information is not available and cannot be obtained from the field personnel, the sample should be invalidated at this point. Visually check the absorber to see if it has 50 mℓ of reagent. If it does not have 50 mℓ, check for signs of leaks and check the Sample Record Sheet for comments by the field operator. If the absorber is low and the field operator's entry on the Sample Record Sheet says that there was 50 mℓ when mailed, continue the analysis. If the absorber is visually low and there are no comments by the field operator on the Sample Record Sheet, invalidate the sample. Also, any 24-hour sample that required more than 15 mℓ of TCM to be added should be invalidated.

Recalibrate the Critical Orifice (Step 11)

Recalibrate the critical orifice in the same manner that it was calibrated originally in Step 2. Record the new K value in the calibration log book. If the final K value differs from the initial K value by more than 10 percent, the sample should be invalidated. Compute the percent deviation by

$$\text{percent difference} = \frac{K_i - K_f}{K_i} \times 100$$

where K_i = the initial K value $(cm^3/min)/(°K)^{1/2}$

and K_f = the final K value $(cm^3/min)/(°K)^{1/2}$.

If the final K value is within 10 percent of the initial K value, compute the average flow rate for the sampling period by:

$$\bar{Q} = \frac{K_i + K_f}{2} (T_f)^{1/2}$$

where $\bar{Q}$ = the average flow rate (cm^3/min),

K_i and K_f = initial and final calibration K values, respectively,

and T_f = average temperature reported by field operator, °K.

Use $\bar{Q}$ in subsequent calculations.

Reagent Preparation For Analysis (Step 12)

Prepare reagents for analysis according to the directions given in Subsection 6.2 of the Appendix. Class A volumetric glassware should be used. The analytical balance should be checked before preparing a batch of reagents by weighing a standard weight between 1 and 3 grams. If the measured and actual weights agree within ± 0.4 mg proceed with the preparation. Record the actual and measured weights in the laboratory log book. If the weights differ by more than ± 0.4 mg, continue the preparation but report to the supervisor that the balance calibration needs checking. This should be carried out by a manufacturer's representative.

Sulfamic Acid (0.6 percent) - Dissolve 0.6 g sulfamic acid in a 100 mℓ volumetric flask with water, and bring to mark. Keep in a glass-stoppered flask while not in use. Prepare fresh daily.

Formaldehyde (0.2 percent) - Dilute 5 mℓ formaldehyde solution (36-38 percent) to 1,000 mℓ with distilled water. Keep in a stoppered container while not in use. Prepare fresh daily.

Stock Iodine Solution (0.1 N) - Place 12.7 g iodine in a 250 mℓ beaker; add 40 g potassium iodide and 25 mℓ of water. Stir until all is dissolved, then transfer to a 1,000 mℓ flask and dilute to the mark with distilled water. Keep the solution in a glass-stoppered, dark, bottle and store in a cool place.

Working Iodine Solution (0.01 N) - Prepare approximately 0.01 N iodine solution by diluting 50 mℓ of stock solution to 500 mℓ with distilled water. Keep in a glass-stoppered, dark, bottle or flask. It is recommended that this solution be prepared fresh from stock daily.

Starch Indicator Solution - Triturate 0.4 g soluble starch and 0.002 g mercuric iodide (preservative) with a little water, and add paste slowly to 200 mℓ boiling water. Continue boiling until solution is clear; cool, and transfer to a glass-stoppered bottle. Alternatively a solution of stabilized starch for volumetric determinations can be purchased commercially.

Stock Sodium Thiosulfate Solution (0.1 N) - Prepare a stock solution by dissolving 25 g sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) in 1,000 mℓ freshly boiled, cooled, distilled water and add 0.1 g sodium carbonate to the solution. Allow the solution to stand 1 day before standardizing. To standardize, accurately weigh to the nearest 0.1 mg, 1.5 g primary standard potassium iodate (KIO_3) dried at 180°C for 1 hour and cooled in a dessicator. Dilute to volume in a 500 mℓ volumetric flask. To a 500 mℓ iodine flask, pipet 50 mℓ of iodate solution, add 2 g potassium iodide and 10 mℓ of 1 N hydrochloric acid. Stopper the flask. After 5 minute titrate with stock thiosulfate solution to a pale yellow. Add 5 mℓ starch indicator solution and continue the titration until the blue color disappears. Calculate the normality of the stock solution as follows:

$$N = \frac{W}{M} \times 2.80$$

where N = normality of stock thiosulfate solution,

M = volume of thiosulfate required, mℓ,

W = weight of potassium iodate, grams,

and $2.80 = \frac{10^3 \text{ (conversion of g to mg)} \times 0.1 \text{ (fraction iodate used)}}{35.67 \text{ (equivalent weight of potassium iodate)}}$

Keep this solution stored in a glass-stoppered bottle or flask.

This solution should not be used without being restandardized if stored for more than one month.

Sodium Thiosulfate Titrant (0.01 N) - Accurately pipet 100 mℓ of the stock thiosulfate solution into a 1,000 mℓ volumetric flask. Dilute to the mark with freshly boiled, cooled distilled water. This 0.01 N solution is not stable, and must be prepared fresh daily from the stock thiosulfate solution. Keep in a glass-stoppered flask or bottle when not in use.

Normality = Normality of stock solution × 0.100.

Standardized Sulfite Solution for Preparation of Working Sulfite - TCM Solution - Dissolve 0.3 g of sodium metabisulfite (Na_2SO_3) in 500 mℓ of recently boiled, cooled, distilled water. (Sulfite solution is unstable; it is therefore important to use water of the highest purity to minimize this instability.) This solution contains the equivalent of 320 to 400 µg/mℓ of SO_2. The actual concentration of the solution is

determined by adding excess iodine and backtitrating with standard sodium thiosulfate solution. To backtitrate, pipet 50 mℓ of the 0.01 iodine into each of two 500 mℓ iodine flasks (A and B). To flask A (blank) add 25 mℓ distilled water, and to flask B (sample) pipet 25 mℓ sulfite solution. Stopper the flasks and allow to react for 5 minutes. Prepare the working sulfite-absorbing reagent solution (see below) at the same time iodine solution is added to the flasks. By means of a buret (50 mℓ buret) containing standardized 0.01 N thiosulfate, titrate each flask in turn to a pale yellow. Then add 5 mℓ of starch solution to the flask and shake thoroughly. Continue the titration until the blue color disappears. Store in a glass-stoppered bottle or flask.

Working Sulfite-TCM Solution - Pipet accurately 2 mℓ of the standard solution into a 100 mℓ volumetric flask and bring to mark with 0.04 M absorbing reagent. Calculate the concentration of sulfur dioxide in the working solution:

$$\mu g\ SO_2/m\ell = \frac{(A-B)(N)(32{,}000)}{25} \times 0.02^*$$

where A = volume thiosulfate for blank, mℓ,

B = volume thiosulfate for sample, mℓ,

N = normality of thiosulfate titrant,

32,000 = milliequivalent weight of SO_2, μg, and

0.02 = dilution factor.

This solution is stable for 30 days if kept at 5°C (refrigerator). If not kept at 5°C prepare fresh daily.

Pararosaniline Reagent - To a 250 mℓ volumetric flask add 20 mℓ stock pararosaniline solution. Add an additional 0.2 mℓ stock solution for each percent the stock assays below 100 percent. Then add 25 mℓ of 3 M phosphoric acid and dilute to volume with distilled water. This reagent stored in a glass-stoppered bottle is stable for at least 9 months.

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*This equation as written in Subsection 6.2.9 of the Appendix is in error by a factor of 25.

Preparing a Purified Pararosaniline Stock Solution - In preparing a purified pararosaniline stock solution the method referenced in Subsection 6.2.10.2 of the Appendix for purifying the dye is as follows (Ref. 2):

(1) Place 100 mℓ each of 1-butanol and 1N HCl in a large separatory funnel (250 mℓ) and allow to equilibrate. Note: Certain batches of 1-butanol contain oxidants that create an SO_2 demand. Before using check by placing 20 mℓ of 1-butanol with 5 mℓ of 20 percent potassium iodide (KI) in a 50 mℓ separatory funnel and shake thoroughly. If a yellow color appears in the alcohol phases, redistill the 1-butanol from silver oxide, and collect the middle fraction, or purchase a new supply of 1-butanol.

(2) Weigh 100 mg of pararosaniline hydrochloride (PRA), in a small beaker. Add 50 mℓ of the equilibrated acid (drain the acid from the bottom of the separatory funnel in (1) above) to the beaker and let stand for several minutes.

(3) To a 125 mℓ separatory funnel, add 50 mℓ of the equilibrated 1-butanol (draw the 1-butanol from the top of the separatory funnel in (1) above). Transfer the acid solution (from (2) above) containing the dye to the funnel, and extract. The violet impurity will transfer to the organic phase.

(4) Transfer the lower (aqueous phase) into another separatory funnel and add 20 mℓ of 1-butanol; extract again.

(5) Repeat the extraction procedure with three more 10 mℓ portions of 1-butanol. This procedure usually removes almost all of the violet impurity that contributes to the blank.

(6) After the final extraction, filter the acid phase through a cotton plug into a 50 mℓ volumetric flask and bring to volume with 1 N HCl. This stock reagent will be yellowish red.

Assaying the Pararosaniline Stock Solution - The concentration of pararosaniline hydrochloride (PRA) need be assayed only once after preparation. It is also recommended that commercial solutions of pararosaniline be assayed when first purchased. The assay procedure is as follows (Ref. 2):

(1) Prepare a buffer stock solution with a pH of 4.69 by dissolving 13.61 g of sodium acetate trihydrate in distilled water in a 100 mℓ volumetric flask. Add 5.7 mℓ of glacial acetic acid and dilute to volume with water.

(2) Take 1 mℓ of the stock solution obtained from the purification process or from a commercial source and dilute to the mark in a 100 mℓ volumetric flask with distilled water.

(3) Transfer a 5 mℓ aliquot to a 50 mℓ volumetric flask. Add 5 mℓ of 1M acetate-acetic acid buffer solution from (1) above and dilute the mixture to the mark with distilled water. Let the mixture set for 1 hour.

(4) Measure the absorbance at 540 nm with a spectrophotometer. Compute the percent of nominal concentration of PRA by

$$\% \text{ PRA} = \frac{A \times K}{W}$$

where A = the measured absorbance of the final mixture (absorbance units),

W = the weight in grams of the dye used in the assay. For example, 100 mg of dye was used to prepare 50 mℓ of solution in the purification procedure and 1 mℓ of the solution was used in the assay, then W = 0.002 g ($\frac{1}{50} \times 100$ mg). When obtained from commercial sources use the stated concentration to compute W.

K = a constant whose value has to be determined for a given spectrophotometer and associated equipment. For example, when using 1-cm optical path length cells, 0.04 mm slit width in a Beckman DU spectrophotometer, K = 21.3.

Note: For other spectrophotometers and equipment, K can be determined by assaying a batch of PRA of known purity (i.e., in the above equation % PRA is known, A and W is measured then K can be calculated).

Develop a Calibration Curve (Step 13)

Procedure With Sulfite Solution - Develop a calibration curve as directed in Subsection 8.2.1 of the Appendix, page 114. Obtain at least 6 data points and construct the best-fit, straight line using the method of least squares. Check the calibration curve to determine if it satisfies the following requirements:

(1) The slope is between 0.03 $\pm$ 0.002 absorbance unit/ µg SO_2. A slope outside these limits indicates that an impure dye or an improperly standardized sulfite solution was used. The calibration should be repeated and if the slope remains outside the above limits, the sulfite solution should be restandardized and the purity of the dye checked to determine the trouble. If necessary, prepare all new reagents and develop a new calibration curve.

(2) The calibration curve intercept on the absorbance axis is between 0.163 $\pm$ 0.039 with the calibration performed at room temperature. The above numbers represent the mean and 3σ values for the calibration curve intercept from a collaborative test of the method (Ref. 6).

If the intercept is outside the above limits and the room temperature is approximately 22°C, the calibration curve should be repeated after checking the spectrophotometer for proper calibration. If the intercept remains outside the above limits, with the temperature ~22°C, chemicals and laboratory procedure should be checked before preparing new reagents and developing a new calibration curve.

The process of checking and repeating should be continued until a calibration curve with an intercept within the above limits is obtained.

(3) Check each calibration point and repeat any point deviating more than 0.8 µg SO_2 (2σ value for measuring control samples from Ref. 6) from the best-fit curve for a given absorbance value. Average the two values and replot the point. Repeat until all points are within 0.8 µg SO_2 of the best-fit curve.

(4) Compute the reciprocal of the slope and record on the calibration curve. File the calibration curve in the calibration log book after having the supervisor accept the results by signing and dating the calibration curve.

A new calibration curve must be developed when:

(1) a new batch of reagents is made, or

(2) a control sample cannot be measured within $\pm$ 1.2 µg SO_2 of its actual value when the control sample is prepared as directed in Subsection 8.2.1 of the Appendix, page 114.

Procedure with SO_2 Permeation Tubes - Procedures for generating standard atmospheres and preparation of a calibration curve are given in Subsection 8.2.2 of the Appendix. SO_2 permeation tubes having nominal shelf lives (at 22°C) ranging from 4 to 24 months are commercially available (Ref. 3). Tubes with a certified permeation rate can be obtained from the National Bureau of Standards (NBS). Alternatively permeation tubes may be prepared and calibration. However, this should only be attempted by experienced personnel in a well-equipped laboratory.

Calibration of SO_2 permeation tubes - A detailed discussion of the required apparatus and procedures for preparation and gravimetric calibration of permeation tubes is given in Reference 4. A method for volumetrically calibrating SO_2 permeation tubes is given in Reference 5. Permeation rates determined both volumetrically and gravimetrically for 4 tubes showed volumetric determinations averaging 3 percent higher than gravimetric determinations (Ref. 5).

The use of either of the above techniques requires a trained/experienced operator, therefore, step-by-step procedures are not attempted here. The operator should refer directly to the above references for guidance.

Calibration check - A permeation tube, whether prepared and calibrated in the laboratory, purchased from a manufacturer with a stated permeation rate, or obtained from the NBS with a certified permeation rate, should be checked periodically throughout its useful lifetime. A permeation tube to be used continuously at a given temperature can be monitored in the following manner.

(1) Equilibrate the tube at the temperature it is to be used.

(2) Weigh the tube to the nearest 0.1 mg with an analytical balance sensitive to 0.01 mg.

    The tube should be handled with teflon-tipped forceps with special care exercised not to expose the tube to dust or other contaminants. Also, any static charge should be removed from the tube.

(3) Record the weight to the nearest 0.1 mg, the date and time of weighing to the nearest minute in the calibration log book for that permeation tube.

(4) The tube should be reweighed at intervals equivalent to 1/10 of the expected life of the tube or, once a month, whichever is shorter.

(5) For each new weighing compute a permeation rate using the previous weighing and the elapsed time. Record this value in the calibration log book.

(6) Compute the percent deviation from the stated or certified value by

$$\text{percent deviation} = \frac{P_a - P_m}{P_a} \times 100$$

where P_a = actual (certified) permeation rate (µg/min)

and P_m = measured permeation rate (µg/min).

With proper handling and use, an SO_2 permeation tube usually maintains a constant permeation rate (at a constant temperature) as long as any liquid is visible in the tube. Therefore, a drop in the permeation rate indicates that the tube has been damaged or that the liquid SO_2 is nearly gone. It is suggested that the certified or stated permeation rate be used as long as the measured rate is within ± 5 percent of the original value. If the measured permeation rate is less than 95 percent of the stated or certified permeation rate, the tube should be replaced if there is little or no liquid SO_2 in the tube. If the tube still has a good supply of liquid SO_2, the new measured permeation rate should be used and the tube reweighed at time intervals equivalent to a weight loss of about 10 mg as computed by the permeation rate until 3 successive measured permeation rates agree within ± 5 percent of the average value of the three. The average value should be used as long as future checks are within ± 5 percent.

Developing a calibration curve - Develop and construct a calibration curve according to the directions given in Subsection 8.2.2 of the Appendix, page 114.

Check each point on the calibration curve and redo any point that deviates more than ± (0.8 µg SO_2) from the best-fit curve. Replot the average of the old and new values and construct a new best-fit curve. Continue the replication until the average of the two most recent measurements falls within ± (0.8 µg SO_2) of the best-fit curve.

Determine the total µg SO_2 in the sample by multiplying the known concentration of the calibration apparatus output (µg SO_2/m^3) times the total volume of calibration air sampled (m^3).

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Compute the reciprocal of the calibration curve slope and record the value on the calibration curve. File the curve in the calibration log book after it has been dated and signed by the supervisor.

A new calibration must be performed when:

(1) a new batch of reagents are prepared, or

(2) when a control sample cannot be measured within $\pm$ (1.2 µg SO_2) of its actual value when prepared with an SO_2 permeation tube.

Colorimetric Analysis (Step 14)

Prepare the sample, reagent blank, and control sample as directed in Subsection 7.2 of the Appendix, page 114.

Set the spectrophotometer to a wavelength of 548 nm. Allow at least 5 minutes for the spectrophotometer to warm up. If necessary, adjust the zero control to bring the meter needle to 0 on the percent transmittance scale. Standardize the light control by inserting a cell filled with distilled water into the sampler holder and adjusting the light control as required, until the meter reads 100 percent transmittance. The complete transmittance scale should be checked with a calibrated set of filters from the National Bureau of Standards any time a control sample cannot be measured with $\pm$ 1.2 µg SO_2 of its known value.

It is recommended that a reagent blank and control sample be measured before each set of determinations. Record the absorbance value of the reagent blank and the total µg SO_2 measured for the control sample in the data log book with the time to the nearest hour. If the absorbance blank is within $\pm$ 0.03 absorbance unit of the calibration curve absorbance intercept and, if the measured value of the control sample is within $\pm$ 1.2 µg SO_2 of the actual value, proceed to analyze the field samples.

If the reagent blank and/or control sample falls outside the above limits the reagent blank, control sample, and calibration curve should be checked by replication as necessary to satisfy the above limits before analyzing field samples.

It is recommended that when first implementing a quality assurance program the pH of the final solution be measured for a sample from each sampling site. If the pH is less than 1.4 or greater than 1.8, the sample should be invalidated and reported to the supervisor. If the pH is between 1.5 and 1.7, accept as good and if the pH is between 1.4 and 1.5, or 1.7 and 1.8, the exact pH value should accompany the reported concentration value for that sample. In any case, checks should be made in an effort to determine why the pH was outside 1.6 $\pm$ 0.1 and corrective action taken.

The pH should seldom, if ever, deviate from 1.6 $\pm$ 0.1, but large errors result if it does. Therefore, it is suggested that the pH of the final solution be checked for 1 sample a month for each sampling site. Report the measured pH to the supervisor and record the pH value with the site identification data in the laboratory log book.

Record all measured values (i.e., reagent blanks, control samples, samples) in sequential order in the data log book. The date and time should be recorded with each set of determinations. The reagent blank should only be used with the set of determinations in which it was measured.

DATA PROCESSING

Perform Calculations (Step 15)

Rotameter - When a rotameter is used to measure the flow rate, perform the following calculations.

(1) Obtain the rotameter reading, I_i and I_f, average temperature, T_f, average pressure, P_f, and sampling period time as reported on the Sample Record Sheet by the field operator.

(2) From the rotameter calibration curve determine the K values for readings of I_i and I_f.

(3) Compute the average flow rate, $\bar{Q}_f$, at field conditions by

$$\bar{Q}_f = \left(\frac{K_i + K_f}{2}\right)\left(\frac{I_i + I_f}{2}\right)\left(\frac{T_f}{P_f}\right)^{1/2}$$

(4) Calculate the volume sampled, V_f, at field conditions by

$$V_f = \bar{Q}_f \times t$$

where t is the sampling period time in minutes.

(5) Correct the sampled volume to volume, V_R, at reference conditions by

$$V_R(\ell) = V_f(cm^3) \times \frac{P_f}{760} \times \frac{298}{T_f + 273} \times 10^{-3}(\ell/cm^3).$$

(6) Compute the average measured SO_2 concentration as directed in Section 9.2 of the Appendix, page 114.

Critical Orifice - When a critical orifice is used to control flow rate perform the following calculations.

(1) Obtain $\bar{Q}$ as computed in Step 11, page 36. Also, obtain the sampling period time, t, the average temperature, T_f, and the average pressure, P_f, as reported by the field operator.

(2) Compute the volue, V_f, sampled at field conditions by

$$V_f = \bar{Q}_f \times t$$

where t is the sampling period time in minutes.

(3) Correct the sampled volume to reference conditions by

$$V_R(\ell) = V_f(cm^3) \times \frac{P_f}{760.} \times \frac{298}{T_f} \quad 10^{-3} \ (\ell/cm^3).$$

(4) Compute the average measured SO_2 concentration in $\mu g/m^3$ as directed in subsection 9.2 of the Appendix, page 114.

Document and Forward Data (Step 16)

Record the average concentration of SO_2 in $\mu g/m^3$ with required identifying information on the appropriate SAROAD Data Form. See Users Manual: SAROAD (Storage and Retrieval of Aerometric Data), APTD-0663, for detailed instructions for accomplishing this. The original calculations should be filed in the operational data log book.

SPECIAL CHECKS FOR AUDITING

Proper implementation and conduct of an auditing program will allow one to estimate data quality in terms of precision and accuracy at a given level of confidence. To realize maximum benefits from an auditing program, it should be conducted independently of the routine operation of the sampling network. That is, checks should be made by individuals other than the regular operator. Furthermore, the checks should be performed without any special preparation or adjustment of the system (see page 96 for further discussion).

It is felt that in conjunction with the special checks given in the operating procedures three audit checks will be sufficient to properly assess data quality. The checks include:

(1) a check of the average flow rate or volume of air sampled for sample collection,

(2) measurement of control samples to evaluate the analysis process, and

(3) a data processing check to evaluate calculation and recording errors.

A checking or auditing level of 7 checks (n = 7) out of 100 sampling periods (N = 100) is used here for illustration purposes when sampling is carried out on a daily basis. For cases where one sample is collected every sixth day, a minimum auditing level of 1 check per month is recommended. This would result in an auditing level of approximately 3 checks (n = 3) for a lot size of 15 (N = 15) for data reported quarterly. The supervisor will specify the auditing level to be used according to local monitoring needs.

Directions for performing each of the checks are given here. Proper use of the resulting data along with desirable control limits are given in the Supervision Manual starting on page 62.

Flow Rate/Volume Check

Volume Check - The volume of air sampled can be checked with a calibrated wet test meter for 30-minute and 1-hour sampling periods with approximate flow rates of 1000 cm^3/m (1 ℓ/min) and 500 cm^3/min (.5 ℓ/min) respectively.

Note: A flow rate of 500 cm^3/min is below the normal range of wet test meters. Hence, the meter must be calibrated at this exact flow rate against a soap-bubble meter. If the meter accuracy varies from check to check by more than ± 2 percent, it should not be used for this low flow rate.

The regular operator prepares the sampler for collecting a sample in the usual manner recording usual site parameters such as temperature and pressure. If a critical orifice is used in the sampling train the person performing the check should provide a calibrated orifice. The sampler is allowed to run for 30-minutes of 1-hour as appropriate.

Compute the volume of air measured by the wet test meter corrected to reference conditions by

$$V_R(C) = V_m \times \frac{P_m}{760} \times \frac{298}{T_m} ,$$

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where $V_R(C)$ = volume measured by wet test meter at reference conditions, ℓ,

V_m = volume measured by wet test meter at T_m and P_m, ℓ,

P_m = barometric pressure plus meter pressure read from the manometer, mmHg,

and T_m = temperature of liquid in wet test meter, °K.

Compute the volume of air sampled as measured by the rotameter/critical orifice and correct to reference conditions according to the procedure in step 15, page 46. Designate this volume as $V_R(0)$.

Compute the percent difference in the two volumes by

$$d = \frac{V_R(C) - V_R(0)}{V_R(C)} \times 100 .$$

Report the values of $V_R(C)$, $V_R(0)$, and d with site identification data, date, and signature of person performing the check to the supervisor.

The sample collected during the check is not a valid sample and should be invalidated and forwarded to the laboratory for safe disposal.

If d from the above calculations is equal to or greater than 9 the sampling train including rotameter/critical orifice should be checked and corrective action taken before sampling is resumed.

Flow-Rate Check - For 24-hour samples a flow-rate check is recommended as a means of auditing the sample collection phase of the measurement process. The check is performed as follows:

(1) The regular operator prepares the sampler for sample collection as usual. This includes filling in the Sample Record Sheet.

(2) The individual performing the audit inserts a calibrated rotameter in the sample inlet line just upstream of the outside filter (see Figure 8).

(3) With the calibrated rotameter in place the sample is collected in the usual manner.

(4) The individual performing the audit reads the calibrated rotameter before, I'_i and after, I'_f, the sampling period and at one point, preferably the midpoint, during the sampling period, I'_m.

(5) Following the procedure given in Step 15, page 46, for rotameters, calculate the volume at reference conditions for the calibrated rotameter, $V_R(C)$. In this case the equation for computing the average flow rate is

$$\bar{Q}_f = \left(\frac{K'_i + K'_m + K'_f}{3}\right)\left(\frac{I'_i + I'_m + I'_f}{3}\right)\sqrt{\frac{T_f}{P_f}} \quad .$$

(6) Compute the sampled volume, $V_R(O)$, measured by the regular rotameter/critical orifice and correct to reference conditions according to the procedure given in Step 15, page 46.

(7) Compute the percent difference by

$$d = \frac{V_R(C) - V_R(O)}{V_R(C)} \times 100 \quad .$$

(8) Record I'_i, I'_m, I'_f, I_i, I_f, and d and forward to the supervisor.

(9) If d is equal to or greater than 9, trouble shooting should be performed and corrective action taken before sampling is resumed.

Measurement of Reference Samples

Measurement of a reference sample prepared independently of normal operations can be used to evaluate the precision and accuracy of the analysis phase of the measurement process. A reference sample as used here refers to a sample prepared by an individual other than the regular operator using reagents prepared independent of those used for normal operations and used for auditing purposes. A control sample as referred to in the operating procedures implies a solution prepared by the regular operator from the normally used reagents and used periodically to verify that the analysis process is under control.

The procedure for performing the check is given below. The frequency of performing the check will be specified by the supervisor. Further discussion is given in the Supervision Manual on page 63.

(1) Prepare a reference sample with a known concentration in the same manner as was used when developing a calibration curve (see Section 8 of the Appendix). The concentration should be varied over the range of normally measured values from audit to audit.

(2) Have the regular operator to measure the reference sample. The operator must not know the true concentration of the reference sample and preferably not know that it is a reference sample.

(3) Obtain the operator's finding $(\mu g\ SO_2)_m$ and the true concentration $(\mu g\ SO_2)_c$ of the sample and compute the difference by

$$d = (\mu g\ SO_2)_m - (\mu g\ SO_2)_c$$

(4) Record $(\mu g\ SO_2)_m$, $(\mu g\ SO_2)_c$ and d and forward to the supervisor.

It is recommended that the supervisor maintain a record of the d values in chronological order and that analysis be stopped, checks made to determine the likely cause(s), and corrective action taken before the analysis is resumed anytime:

(a) a d value equal to or greater than 1.2 $\mu g\ SO_2$ is observed,

(b) two consecutive d values (i.e., results from two consecutive audit checks) exceed $\pm$ 0.8 $\mu g\ SO_2$ in the same direction, or

(c) three consecutive d values (i.e., results from three consecutive audit checks) exceed $\pm$ 0.4 $\mu g\ SO_2$ in the same direction.

(5) If the control sample measurement was outside the above limits, the calibration curve should be checked by measuring a reagent blank and control sample. If necessary, a new calibration curve should be developed and other corrective actions taken as deemed necessary.

After corrections are made, a new reference sample should be measured and, if acceptable, analysis resumed.

(6) If the supervisor reports that the reference sample measurement of (4) above was within limits, continue normal operations.

Data Processing Check

In auditing data processing procedures, it is convenient and allows for corrections to be made immediately if checks are made soon after the original calculations have been performed. In particular, this allows for possible retrieval of additional explanatory data from field personnel when necessary.

The check must be independent; that is, performed by an individual other than the one who originally reduced the data. The check is made starting with the raw data and continuing through recording the concentration in $\mu g/m^3$ on the SAROAD form.

If the mass concentration of SO_2 computed by the check differs from the original value by as much as $\pm$ 3 percent, all samples collected since the previous audit are checked and corrected. The check value is always reported as the correct value.

Record the check and original values in the operational data log book and report the values to the supervisor.

SPECIAL CHECKS TO DETECT AND IDENTIFY TROUBLE

The following checks are recommended as a means of checking the adequacy of different phases of the measurement process. The checks are:

(1) estimate the average temperature environment experienced by a sample between collection and analysis,

(2) interference checks,

(3) measurement of the pH of the final solution at time of analysis,

(4) visual check of the volume of absorbing reagent in the exposed absorber before analysis, and

(5) a check on the accuracy of the sampler timer.

Errors resulting from any one of the above areas would not be detected by the auditing process. However, errors from all except the first source should be small if the suggested operating procedures are being followed. Checks 2 through 5 should be performed for each sampling site when:

(1) a quality assurance program is first initiated in order to identify potential problem areas, and

(2) periodically thereafter by the supervisor as an overall check on the measurement process.

Check number 1 should be made for each site when:

(1) a quality assurance program is first initiated, and

(2) when any change in sample handling or shipping occurs.

Average Temperature Environment of Sample Between Collection and Analysis

For samples that spend several days in transit from the sampling site to the analysis laboratory, the loss of SO_2 at elevated temperatures can be significant (Ref. 2). From the geographical location of the site and laboratory, the season of the year, and the mode of transport make a rough estimate of the average temperature that the sample will be exposed to from the completion of the sampling period to the time of analysis. It is recommended that the following corrections be applied to the measured concentration at reference conditions for any sample with an unrefrigerated time lapse greater than 1 day between collection and analysis:

(1) If the estimated average temperature is 5°C or less no correction is necessary.

(2) If the estimated average temperature is between 5 and 22°C the corrected concentration should be calculated by (Ref. 2)

$$(\mu g\ SO_2/m^3)_c = \frac{(\mu g\ SO_2/m^3)_m}{1.0 - 0.01 \times D}$$

where $(g\ SO_2/m^3)_c$ = the corrected concentration of SO_2,

$(g\ SO_2/m^3)_m$ = the measured concentration of SO_2,

and D = the elapsed time between collection and analysis in days.

(3) If the estimated average temperature is between 22 and 28°C the corrected concentration is calculated by (Ref. 7)

$$(\mu g\ SO_2/m^3)_c = \frac{(\mu g\ SO_2/m^3)_m}{1.0 - 0.02 \times D}\ .$$

These corrections are only rough estimates. The most desirable situation would be to have D very small or the temperature controlled at a known level.

Measurement of pH of Final Solution

The absorbance of a sample is highly sensitive to the solution pH (Ref. 2). Therefore, it is suggested that samples from each site be checked initially to determine if the ambient atmosphere contains pollutants in sufficient quantities to affect the pH of the final solution and thereafter as a check on the reagents used in the analysis when control samples cannot be measured within specified limits. The pH should be measured just prior to the analysis. Any sample having a pH outside of 1.6 $\pm$ 0.1 should be investigated and corrective action taken. The primary suspect would be an error in the quantity of phosphoric acid added to the sample.

Interference Checks

Control samples and reference samples with known concentrations of SO_2 are measured to evaluate the analysis phase of the measurement process. In addition to those measurements, it is recommended that periodically reference samples be spiked with one or more of the principal known interferences to evaluate the effectiveness of chemicals and procedures used to reduce or eliminate the interference.

Spiked samples should be used when the ambient atmosphere is known to contain higher than normal concentrations of a particular interference or any time the reported SO_2 values appear larger than expected from a set of determinations.

One means of performing the check is as follows:

(1) Prepare two control samples with identical amounts of the working sulfite-absorbing reagent solution (see Subsection 6.2.9 in the Appendix).

(2) Spike one of the control samples with a known quantity of the interference of interest.

   (a) Nitrates or nitrites can be used to prepare a solution of known concentration of nitrogen oxides.

   (b) Salts of the heavy metal of interest can be used to prepare solutions of known concentrations for spiking the control sample.

(3) Have the operator measure a reagent blank, the unspiked control sample, and the spiked control sample in sequence.

(4) Compare the measured concentration of the two control samples by computing the difference

$$\text{difference} = (\mu g\ SO_2)_2 - (\mu g\ SO_2)_1$$

where $(\mu g\ SO_2)_1$ = total measured concentration of the unspiked sample,

$(\mu g\ SO_2)_2$ = total measured concentration of the spiked sample.

(5) If the difference is equal to or less than $\pm$ 1.2, it is assumed that there is no difference in the sample.

(6) If the percent difference is greater than the above limits the appropriate chemicals and procedures should be checked and corrective action taken to eliminate interferences.

Volume of Absorbing Reagent

An error in the volume of sample prior to analysis is transferred directly to the measured concentration.

The operator removing the absorber from the sampling train is responsible for replacing any absorbing reagent that was evaporated during sample collection for 24-hour samples that have to be mailed to the laboratory. The operator performing the analysis is responsible for bringing the sample volume to the specified amount for samples delivered directly to the laboratory from the field site.

Absorbers and associated Sample Record Sheets should be checked periodically just prior to analysis to determine if the sample volumes are accurate and to see if the operating procedures are being followed.

Check of Sample Timer

In 24-hour samples an error of $\pm$ 14 minutes represents an error in the measured concentration of only 1 percent. However, accurate timing is essential for 30-minute and 1-hour samples. If automatic timers are used for the shorter time periods, it should be checked at least every six months against a calibrated time piece such as a stop watch. Alternatively, an elapsed time indicator could be used in conjunction with an uncalibrated timer.

Any deviation in the sample period time as measured by the standard and that indicated by the regular means of measuring the time greater than ± 1 percent from the standard timer should result in replacing the timer or employment of a new technique for measuring the sampling period time.

FACILITY AND APPARATUS REQUIREMENTS

Facility

Primary facilities required for the pararosaniline method are a central laboratory and individual sampling stations. The laboratory should be equipped for

(1) reagent preparation,

(2) storage of chemicals and reagents

(3) calibration of critical orifices or rotameters, and

(4) sample analysis.

The laboratory should be equipped with an automatic all-seasons air conditioning unit capable of maintaining a pre-set temperature within ± 3°C (5°F). It should also be equipped with a hood and exhaust fan large enough to accomodate the acid bath used for cleaning the glassware.

The sample collection unit should include a dark box for housing the bubbler and protecting it from direct sunlight. Also, the box should be thermostated to prevent condensed moisture from freezing in the sampling train lines in cold weather.

Apparatus

Items of equipment with approximate costs are listed in Table 1. Each item is checked according to whether it is 1) required in the reference method, 2) used to control a variable or parameter, 3) required for auditing purposes, or 4) used to monitor a variable. The permeation tube setup is included as an alternate calibration method.

Table 1. APPARATUS USED IN THE MANUAL PARAROSANILINE METHOD

Item of equipment	Approx. cost 1973	Assoc. error	Ref. method	Variable Monitoring	Auditing equipment
CALIBRATION					
1. Flow-rate calibration unit	300	Calibration	✓		
2. Wet test meter	1,000	Calibration			✓
3. Permeation tube calibration setup	2,200	Calibration			
4. Spectrophotometer calibration unit	100	Calibration			
5. Set of standard weights	110	Calibration		✓	
6. Soap bubble meter	50	Calibration			✓
SAMPLING					
7. 24-hr sampling system	250		✓		
8. 30-min/1-hr sampling system	250		✓		
9. 24-hr timer	40		✓		
10. Midget impinger	10		✓		
11. 100 mℓ threaded bubbler	4		✓		
12. Filter holder	2		✓		
ANALYSIS					
13. Spectrophotometer (manual)	600-900		✓		
14. Analytical balance	1,400		✓		
15. pH meter and probe	350			✓	
16. Misc. glassware	100				
17. Reagents (cost/100 samples)	10		✓		

SECTION III SUPERVISION MANUAL

GENERAL

Consistent with the realization of the objectives of a quality assurance program as given in Section I, this manual provides the supervisor with brief guidelines and directions for:

(1) the collection and analysis of information necessary for the assessment of high volume data quality,

(2) isolating, evaluating, and monitoring major components of system error,

(3) changing the physical system to achieve a desired level of data quality,

(4) varying the auditing or checking level to achieve a desired level of confidence in the validity of the outgoing data, and

(5) selecting monitoring strategies in terms of data quality and cost for specific monitoring requirements.

This manual provides brief directions that cannot cover all situations. For somewhat more background information on quality assurance see the Management Manual of this document. Additional information pertaining to the Pararosaniline Method can be obtained from the final report for this contract and from the literature referenced at the end of the Management Manual.

Directions are written in terms of a 24-hour sampling period with reference to 30-minute and 1-hour sampling periods when appropriate and an auditing level of n=7 checks out of a lot size of N=100 for illustration purposes. Special instructions for auditing operations where sampling is performed every sixth day are given also. Information on additional auditing levels is given in the Management Manual.

Specific actions and operations required of the supervisor in implementing and maintaining a quality assurance program as discussed in this Manual are summarized in the following listing.

(1) Data Assessment

(a) Set up and maintain an auditing schedule.

(b) Qualify audit results (i.e., insure that checks are independent and valid).

(c) Perform necessary calculations and compare with suggested performance standards.

(d) Make corrections or alter operations when standards are exceeded.

(e) Forward acceptable qualified data, with audit results attached, for additional internal review or to user.

(2) Routine Operations

(a) Obtain from the operator immediate reports of suspicious data or malfunctions. Initiate corrective action or, if necessary, specify special checks to determine the trouble; then take corrective action.

(b) On a daily basis, evaluate and dispose of (i.e., accept or reject) data that have been identified as questionable by the operator.

(c) Examine operator's log books periodically for completeness and adherence to operating procedures.

(d) Approve sample record data sheets, calibration data, etc., for filing by operator.

(e) File auditing results.

(3) Evaluation of Operations

(a) Evaluate available alternative monitoring strategies in light of your experience and needs.

(b) Evaluate operator training/instructional needs for your specific operation.

ASSESSMENT OF DATA QUALITY

Procedures for implementing and maintaining an auditing program to assess data quality are presented in this section. Throughout this discussion and the rest of this document, the term "lot" is used to represent a set or collection of objects (e.g., measurements or observations), and the "lot size" designated as N is the number of objects in the lot. The number of objects in the lot to be tested or measured is called the "sample size" and is designated as n. The term "auditing level," used interchangeably with "checking level," is fully described by giving the sample size, n, and the lot size, N.

A valid assessment of a lot of SO_2 data generated with the manual pararosaniline method can be made at a given level of confidence with information derived from special checks of key operations in the measurement method. Figure 15 summarizes the quality control checks applied at various check points in the measuring process. Each check or operation is represented by a box. They are in the order in which they would be performed on a particular sample as it progresses through the process.

Boxes enclosed by heavy lines represent 100 percent sampling; i.e., these checks are made on each sample passing through the system. The two checks enclosed by dashed lines are not scheduled at any given rate but are carried out as specific events take place (e.g., a new batch of absorbing reagent is prepared or at the beginning of a set of determinations). The remaining three checks are to be performed at the prescribed auditing level.

All but one of the checks are treated on a go/no-go basis. That is, a standard or limit is defined and the lot or individual item is accepted or rejected on the basis of the check results. Certain rejected lots or samples are corrigible; i.e., they are capable of being corrected. Specifically, samples are corrected for delay between collection and analysis and lots rejected because of data processing errors are accepted after the errors have been located and corrected. The one check not treated on a go/no-go basis is the volume/flow-rate check. This check is performed at the prescribed auditing level. Action for correcting system deficiencies may be taken as the result of any one check, however, there is usually no clear-cut way of correcting previous data. Therefore, results of this check are reported and used in assessing data quality along with the results from measuring reference samples as described in the Management Manual, page 96. Also, in some instances results from the data processing checks may be requested by the manager.

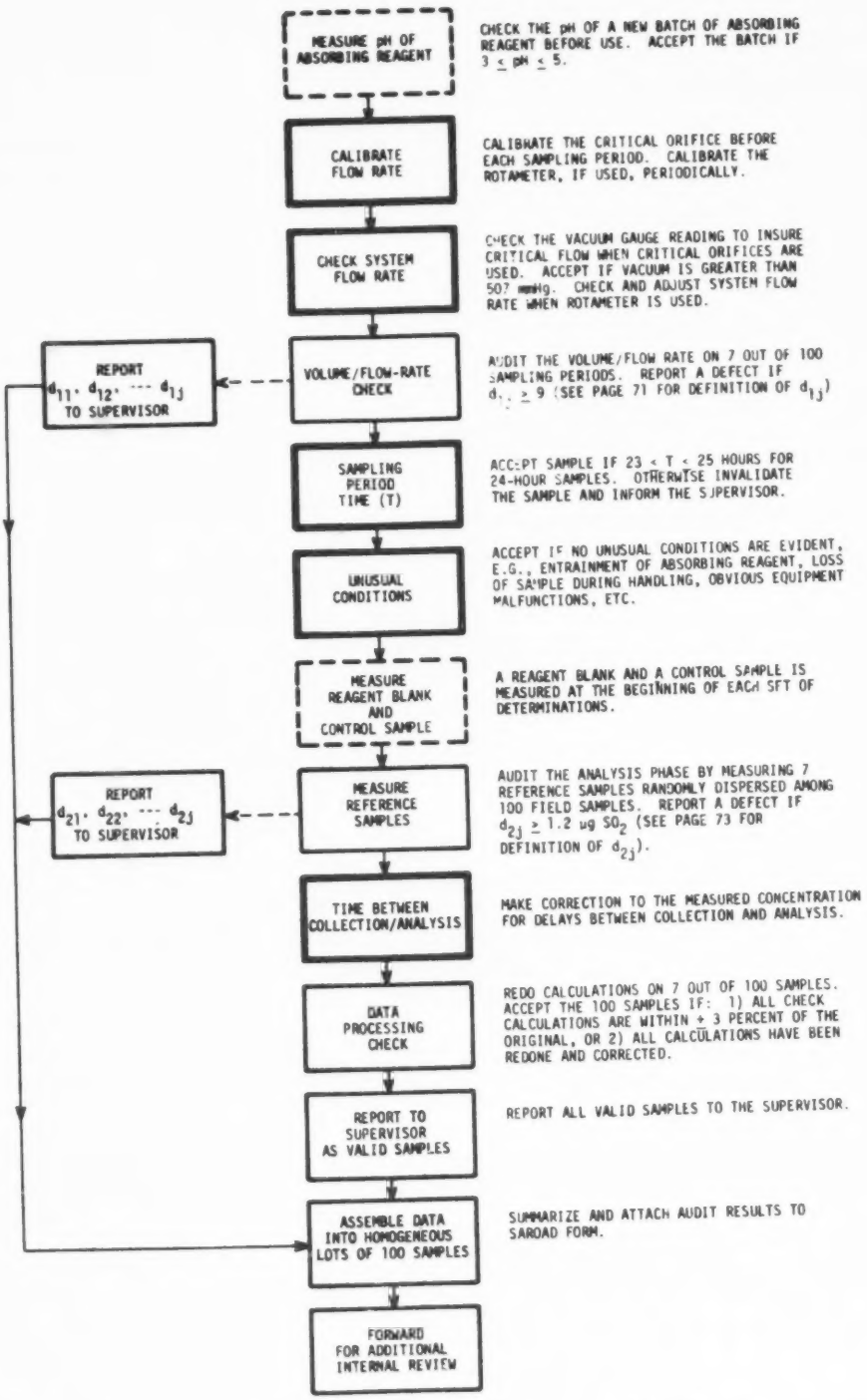
MEASURE pH OF ABSORBING REAGENT
CHECK THE pH OF A NEW BATCH OF ABSORBING REAGENT BEFORE USE. ACCEPT THE BATCH IF 3 ≤ pH ≤ 5.
CALIBRATE FLOW RATE
CALIBRATE THE CRITICAL ORIFICE BEFORE EACH SAMPLING PERIOD. CALIBRATE THE ROTAMETER, IF USED, PERIODICALLY.
CHECK SYSTEM FLOW RATE
CHECK THE VACUUM GAUGE READING TO INSURE CRITICAL FLOW WHEN CRITICAL ORIFICES ARE USED. ACCEPT IF VACUUM IS GREATER THAN 507 mmHg. CHECK AND ADJUST SYSTEM FLOW RATE WHEN ROTAMETER IS USED.
VOLUME/FLOW-RATE CHECK
AUDIT THE VOLUME/FLOW RATE ON 7 OUT OF 100 SAMPLING PERIODS. REPORT A DEFECT IF $d_{1j} \geq 9$ (SEE PAGE 71 FOR DEFINITION OF d_{1j})
REPORT $d_{11}, d_{12}, \cdots d_{1j}$ TO SUPERVISOR
SAMPLING PERIOD TIME (T)
ACCEPT SAMPLE IF 23 < T < 25 HOURS FOR 24-HOUR SAMPLES. OTHERWISE INVALIDATE THE SAMPLE AND INFORM THE SUPERVISOR.
UNUSUAL CONDITIONS
ACCEPT IF NO UNUSUAL CONDITIONS ARE EVIDENT, E.G., ENTRAINMENT OF ABSORBING REAGENT, LOSS OF SAMPLE DURING HANDLING, OBVIOUS EQUIPMENT MALFUNCTIONS, ETC.
MEASURE REAGENT BLANK AND CONTROL SAMPLE
A REAGENT BLANK AND A CONTROL SAMPLE IS MEASURED AT THE BEGINNING OF EACH SET OF DETERMINATIONS.
MEASURE REFERENCE SAMPLES
AUDIT THE ANALYSIS PHASE BY MEASURING 7 REFERENCE SAMPLES RANDOMLY DISPERSED AMONG 100 FIELD SAMPLES. REPORT A DEFECT IF $d_{2j} \geq 1.2$ µg SO_2 (SEE PAGE 73 FOR DEFINITION OF d_{2j}).
REPORT $d_{21}, d_{22}, \cdots d_{2j}$ TO SUPERVISOR
TIME BETWEEN COLLECTION/ANALYSIS
MAKE CORRECTION TO THE MEASURED CONCENTRATION FOR DELAYS BETWEEN COLLECTION AND ANALYSIS.
DATA PROCESSING CHECK
REDO CALCULATIONS ON 7 OUT OF 100 SAMPLES. ACCEPT THE 100 SAMPLES IF: 1) ALL CHECK CALCULATIONS ARE WITHIN ± 3 PERCENT OF THE ORIGINAL, OR 2) ALL CALCULATIONS HAVE BEEN REDONE AND CORRECTED.
REPORT TO SUPERVISOR AS VALID SAMPLES
REPORT ALL VALID SAMPLES TO THE SUPERVISOR.
ASSEMBLE DATA INTO HOMOGENEOUS LOTS OF 100 SAMPLES
SUMMARIZE AND ATTACH AUDIT RESULTS TO SAROAD FORM.
FORWARD FOR ADDITIONAL INTERNAL REVIEW

FIGURE 15: FLOW CHART OF QUALITY CONTROL CHECKS IN THE AUDITING PROGRAM

Required Information

For an auditing program as described above the required information for evaluating data quality includes results from the following checks:

(1) volume/flow-rate checks,

(2) reference sample measurement, and if requested,

(3) data processing checks.

Directions for performing the above checks are given in the Operations Manual, page 47. Directions for insuring independence and proper randomization in the auditing process and for the evaluation of the results are presented in this section.

Collection of Required Information

Volume/Flow-Rate Check - A volume check using a wet test meter is recommended for samples where the flow rate is 500 cm^3/min. or greater. A flow-rate check using a calibrated rotameter is recommended for samples where the flow-rate is less than 500 cm^3/min. procedure for performing the check. Samples from individual sites should be combined into lots. For sites where 50 or more samples are collected each quarter, a minimum of 7 randomly spaced checks per quarter is recommended. A minimum of 3 checks per quarter is recommended for sites operating every sixth day, thereby generating 15 or less samples a quarter.

Randomly select 7 sampling periods from the coming quarter for sites where the lot size is expected to be as large as 50. Record dates. The operator should not be aware of when the checks are to be performed. Remember that when volume checks are made the sample is invalid. Hence, the check should be made before or after the regular sample is collected. The flow-rate check can be made on the actual sample.

For sites where the lot size is 15 or less, randomly select 1 sampling period each month. Record these dates and perform the checks as scheduled. Directions for performing the check are given in the Operations Manual, page 47.

Treatment of data - Obtain the audit results from the individual performing the audit (see Section on "Special Checks for Auditing," page 47).

Using the check value, V_{cj} and the value determined by the operator, V_{oj}, compute the percentage difference by

$$d_{1j} = \frac{V_{cj} - V_{oj}}{V_{cj}} \times 100$$

where V_{cj} = the Volume measured by the wet test meter (corrected to reference conditions) for the j^{th} check performed during an auditing period,

V_{oj} = the Volume measured by the regular method (i.e., flow rate times the sampling period time),

and d_{1j} = the percent difference in the volumes measured for the j^{th} check, the subscript 1 identifies the check as being a volume or flow-rate check.

Report d_{11}, d_{12}, d_{13}, d_{14}, d_{15}, d_{16}, d_{17} and the auditing level on the form in Figure 16, page 65.

Measurement of Reference Samples - Reference samples prepared independent of the normal operations are used to evaluate the analysis phase of the measurement method.

Generation of reference samples - Reference samples should be made using a working sulfite-TCM solution (see Subsection 6.2.9 in the Appendix) that was prepared independent, both personnel and chemicals, from the regularly used solution. Alternatively, reference samples can be prepared with an SO_2 permeation tube set up as shown in Figure A2 and A3 of the Appendix, page 116. Reference samples should span a range from 0.20 to 1.0 absorbance units. The specific values should be varied from audit to audit.

Procedure for performing check - The operator routinely measures 1 control sample, that he has prepared, for every set of determinations as a check on the continued reliability of the calibration curve. The measurement of independent reference samples evaluates the overall analysis procedure including operator, chemicals, and technique.

Reference samples should be dispersed randomly throughout the samples awaiting analysis at the rate of 7 reference samples per 100 field samples. This auditing level can be followed as long as a total of 100 samples will be analyzed per quarter. If possible the reference samples should not be recognizable to the analyst as a reference sample.

Treatment of data - Obtain from the person that performed the audit (see page 44) the measured, $(\mu g\ SO_2)_m$, and check on known value, $(\mu g\ SO_2)_c$ and compute the difference

$$d_{2j} = (\mu g\ SO_2)_{cj} - (\mu g\ SO_2)_{mj}$$

where j is the j^{th} time that the check has been made during a given auditing period.

Data Processing Check - Independent checks on data processing errors are made as directed in the Operations Manual, page 52.

Procedure for performing check - A data processing check should be made on 7 out of 100 samples. The check should be made by an individual other than the operator who performed the original calculations. The check should begin with the raw data through the point of recording the concentration on the SAROAD form.

Treatment of data - Compute the percent difference between the check value, $(\mu g\ SO_2/m^3)_c$, and the original value, $(\mu g\ SO_2/m^3)_o$, by

$$d_{3j} = \frac{(\mu g\ SO_2/m^3)_c - (\mu g\ SO_2/m^3)_o}{(\mu g\ SO_2/m^3)_c} \times 100$$

where j is the j^{th} time that the check has been made during a given auditing period.

Treatment of Collected Information

Identification of Defects - One procedure for identifying defects is to evaluate auditing checks in pairs; i.e., d_{11} d_{21}, d_{12} d_{22}, d_{13} d_{23}, ..., d_{17} d_{27}. If one or both members of the pair are defective, it counts as one defect. No more than one defect is declared per set. Data processing errors should be corrected when found, and are not, therefore discussed here.

Any set of auditing checks in which the value of d_{1j} or d_{2j} is greater than $\pm$ 9 or $\pm$ 1.2 µg SO_2 respectively, will be considered a defect. These values are assumed to be the 3σ values and are discussed in the subsection on Suggested Standards for Judging Performance on page 66. As field data become available, these limits should be reevaluated and adjusted, if necessary.

Reporting Data Quality - Each lot or quarter of data submitted with SAROAD forms or tapes should be accompanied by the minimum data qualifying information as shown in Figure 16. The individual responsible for the quality assurance program should sign and date the form. As an illustration, values from the subsection on Suggested Standards for Judging Performance, page 66, are used to fill in the blanks in Figure 16. The reported auditing rate is the rate in effect at the beginning of the auditing period. An increase or decrease in auditing rate during the auditing period will be reflected by the total number of checks reported. The reason for change should be noted on the form.

Supervisor's Signature_____ Reporting Date_____

Auditing Rate for Data Errors: n = 7, N = 100

Definition of Defect: $|d_{1j}| \geq 9$,

$|d_{2j}| \geq 1.2$ µg SO_2

and $|d_{3j}|^{*} \geq 3$

Number of Defects Reported_____ (should be circled in the table below)

Audit	Check Values				
1. Volume/Flow-Rate Check (d_{1j})	d_{11}	d_{12}	d_{13}	- - -	d_{1n}
2. Measurement of Reference Samples (d_{2j})	d_{21}	d_{22}	d_{23}	- - -	d_{2n}
3. Data Processing Check (d_{3j})	d_{31}	dd_{32}	d_{33}	- - -	d_{3n}

*Data processing errors are corrected when found at the ± 3 percent level and are therefore, not reported as defects.

Figure 16: Data Qualification Form

Check values (i.e., d_{1j}'s, d_{2j}'s and d_{3j}'s) are calculated as directed on pages 62 and 63 and reported in Figure 16. Values of d_{3j} need be reported only if requested by the manager. All reported check values exceeding the definition of a defect should be marked for easy recognition by circling on the form. In case of a defect from the measurement of reference samples (d_{2j}) report the defective measurement as well as the measurement made after the trouble is corrected. Both values would be in the same column of Figure 16 (i.e., two values of one d_{2j} would be reported) with the defect circled. The other value will be used in evaluating data quality as described in the Management Manual, page 96.

SUGGESTED STANDARDS FOR JUDGING PERFORMANCE USING AUDIT DATA

Results from a collaborative test of the pararosaniline method (Ref. 6) show that precision is a function of the SO_2 concentration. The performance standard given below in Table 2 for measurement of reference samples represents the 3σ value from that test. This standard should be reevaluated and adjusted as field data become available.

The suggested standard for comparing the volume/flow-rate values is no more than a rough estimate. There is the error associated with the initial and final calibration of the critical orifice and the accuracy of the wet test meter. Under field conditions a standard deviation of $\pm$ 3 percent of the actual value seems reasonable. Again this standard should be reevaluated as field data become available.

COLLECTION OF INFORMATION TO DETECT AND/OR IDENTIFY TROUBLE

In a quality assurance program one of the most effective means of preventing trouble is to respond immediately to reports from the operator of suspicious data or equipment malfunctions. Application of proper corrective actions at this point can reduce or prevent the collection of poor quality data. Important error sources, methods for monitoring variables, and suggested control limits for each source are discussed in this section.

Identification of Important Parameters

Measurement of sulfur dioxide in the ambient atmosphere by the manual pararosaniline method requires a sequence of operations and events that yield as an end result a number that serves to represent the average mass of sulfur dioxide per unit volume of air over the sampling period.

The measurement process can be roughly divided into three phases. They are: 1) sample collection, 2) sample analysis, and 3) data processing.

Table 2. SUGGESTED PERFORMANCE STANDARDS

Standards for Defining Defects

1. Volume/Flow-Rate Check; $|d_{1j}| \geq 9$

2. Measurement of Reference Samples; $|d_{2j}| \geq 1.2$ µg SO_2

Standard for Correcting Data Processing Errors

3. Data Processing Check; $|d_{3j}| \geq 3$

Standards for Audit Rates

4. Suggested minimum auditing rates for data error; number of audits, n = 7; lot size, N = 100; allowable number of defects per lot, d = 0.

Standards for Operation

5. If at any time d = 1 is observed (i.e., a defect is observed) for either d_{1j} or d_{2j}, increase the audit rate to n = 20, N = 100 until the cause has been determined and corrected.

6. If at any time d = 2 is observed (i.e., two defects are observed in the same auditing period), stop collecting data until the cause has been determined and corrected. When data collection resumes, use an auditing level of n = 20, N = 100 until no defects are observed in three successive audits.

7. If at any time either one of the two conditions listed below is observed, 1) increase the audit rate to n = 20, N = 100 for the remainder of the auditing period, 2) perform special checks to identify the trouble area, and 3) take necessary corrective action to reduce error levels. The two conditions are:

   (a) two (2) d_{1j} values exceeding ± 6, or
   four (4) d_{1j} values exceeding ± 3.

   (b) two (2) d_{2j} values exceeding ± 0.8 µg SO_2, or
   four (4) d_{2j} values exceeding ± 0.4 µg SO_2.

Sample Collection - The sample collection phase of the measurement method contains numerous sources of error. Some errors can be eliminated by a conscientious operator, while others are inherent and can only be controlled. The sources of error are:

(1) flow-rate calibration,

(2) determination of the volume of air sampled,

(3) elapsed time between sample collection and analysis,

(4) exposure of sample to direct sunlight, and

(5) entrainment or loss of sample other than by evaporation.

Flow-rate calibration - Flow rates for critical orifices calibrated against a wet test meter at different times, by different individuals, but with the same equipment showed a standard deviation of less than 2 percent of the mean (Ref. 1). When a large population of laboratories is considered, the variability would undoubtedly increase significantly. Rotameter calibrations would not be expected to be any more precise than critical orifice calibrations. Large flow-rate calibrations will be detected by the volume/flow-rate check as part of the auditing procedure. However, to maintain the error at or near a minimum the wet test meter or calibrated rotameter used for calibration should be checked against a high quality soap-bubble meter at least once a quarter.

Determination of the volume of air sampled - The volume of air sampled is estimated from the calibration of the critical orifice before and after sampling (flow-rate readings before and after sampling if a rotameter is used) and the sampling period time. Such estimate assumes that any change in flow rate during the sampling period is linear with time. Nonlinear changes due to such things as temporary plugging of the line or critical orifice from condensed moisture are not detected by this method. Also, a system leak between the absorber and the critical orifice would introduce an error in the calculated volume unless detected and corrected by the operator prior to sample collection.

Errors in the calculated volume are checked as part of the auditing process by using a wet test meter on-site to measure the integrated volume. A discrepancy in the integrated volume measured by the wet test meter and the volume calculated in the usual manner implies that there could be:

(1) system leaks,

(2) non-linear changes in flow-rate,

(3) an error in the timer, or

(4) flow-rate calibration error.

Each item should be checked and verified.

For the 24-hour sampling period where a calibrated rotameter is used to read the flow rate before, during, and after the sampling period, only items (1) and (4) above can be detected. There is only a small possibility of detecting a temporary change in flow rate (item 2). The timer should be checked independently against an elapsed time indicator at least every six months.

An additional source of error in estimating the sample volume is due to the inability to determine an average temperature for the sampling period. This is more important for 24-hour samples than it is for the shorter periods. A method for estimating the average temperature is suggested in the Operations Manual, page 34.

Elapsed time between sample collection and analysis - It has been shown that exposure of the sample to temperatures above about 5°C results in SO_2 losses. A loss of about 1.8 percent per day occurred at 25°C and no losses were observed at 5°C (Ref. 2).

It is obvious that long delays between sample collection and analysis at unrefrigerated or uncontrolled conditions will result in sizeable errors.

Every means should be employed to minimize the time that a sample is exposed to temperatures above 5°C.

Exposure of sample to direct sunlight - Exposure of the sample to direct sunlight during or after collection can result in deteoriation of the sample. Losses from 4 to 5 percent were experienced by samples exposed to bright sunlight for 30 minutes (Ref. 2). Therefore, it is recommended that the bubbler be wrapped in tin foil anytime it is exposed to the direct sunlight for more than 1 or 2 minutes that might occur in the normal transfer of 24-hour samples from the sampling train box to the shipping block.

Entrainment or loss of sample - Any loss of sample other than evaporation during sample collection should result in the operator invalidating the sample. Large errors can result when:

(1) the operator fails to distinguish between sample loss and evaporation and brings the absorber to the mark with fresh TCM,

(2) the operator fails to bring the absorber to the mark and the laboratory assumes that he did, when in fact part of the sample was lost during shipment, or

(3) the operator is careless in bringing the absorber to the mark (e.g., $\pm$ 1 mℓ represents a 2 percent error in a 24-hour sample).

The supervisor of the analysis section should periodically, visually check the incoming absorbers for accuracy of volume. Also, the field operators should record on the Sample Record Sheet the amount of TCM added or an estimate of how much TCM is needed if he cannot fill it before delivery to the laboratory for analysis.

Sample Analysis - To realize a high level of precision and accuracy from the analysis phase of the method the analyses must be done carefully, with close attention to temperature, pH of final solution, purity of the chemicals and water, and standardization of the sulfite solution (Ref. 2).

Important parameters in the analysis phase include:

(1) purity of the chemicals and water,

(2) spectrophotometer calibration,

(3) pH of the solution being analyzed, and

(4) temperature at analysis compared to temperature at calibration.

Purity of chemicals and water - Purity of the chemicals and water is extremely important in obtaining reproducible results because of the high sensitivity of the method. As recommended in the Operations Manual the purity of the pararosaniline dye is checked and, if necessary, purified and assayed before use. The water used must be free of oxidants and should be double-distilled when preparing and protected from the atmosphere when stored and transferred from container to container. All other chemicals should be ACS grade and special care exercised not to contaminate the chemicals while in storage or when removing portions for reagent preparation.

Spectrophotometer calibration - The spectrophotometer should be adjusted for 100 percent transmittance when measuring a sample cell of pure water prior to each set of determinations. Also, the calibration of the wavelength scale and the transmittance scale should be checked periodically or any time reference samples cannot be measured within prescribed limits after checks of the reagents and water have failed to identify the trouble.

The calibration of the wavelength scale can be checked by plotting the absorption spectrum (in the visible range) of a didymium glass which has been calibrated by the National Bureau of Standards.

The transmittance scale can be checked using a set of filters from the National Bureau of Standards.

pH of the solution being analyzed - For this method the maximum sensitivity occurs when the pH of the final solution is in the region 1.6 ± 0.1 (Ref. 2). If care is exercised in reagent preparation and the analysis phase the pH should always be within the above limits. Phosphoric acid provides the pH control; hence, it should be checked first when the pH is detected outside the above range.

Temperature - Temperature affects the rate of color formation and fading of the final color. Also, the reagent blank has a very high temperature coefficient. Therefore, it is important that the temperature at analysis be within ± 2°C of the temperature at which the calibration curve was developed. If the normal room temperature varies more than ± 2°C from a set value it is recommended that a constant-temperature bath be used if a high degree of accuracy is desired.

Large variations in temperature would be detected as error in measuring control samples and/or reference samples.

Data Processing - Data processing, starting with the raw data through the act of recording the measured concentration on the SAROAD form, is subject to many types or errors. The approach used in the Operations Manual, page 52 means that one can be about 55 percent confident that no more than 10 percent of the reported concentrations are in error by more than ± 3 percent.

The magnitude of data processing errors can be estimated from, and controlled by, the auditing program through performance of periodic checks and making corrections when large errors are detected. A procedure for estimating the bias and standard deviation of data processing errors is given in the Management Manual, page 98.

How to Monitor Important Parameters

Table 3 lists some of the parameters that need to be monitored when using the manual pararosaniline method for measuring atmospheric SO_2. Excess error attributable to one or more of variables 1, 2, 6, 7, 8, and 9 will be detected by the auditing program. Variable 3, elapsed time between sample collection and analysis is determined for each sample as part of the normal operating procedures. Variables 3 and 4 involve an operation or subjective decision by the field operator. They can only be monitored by observing the operator on-site. This can be carried out in conjunction with the performance of the volume/flow-rate audit.

Suggested Control Limits

Appropriate control limits for individual variables will depend on the level of performance needed. Table 4 gives suggested performance standards for measuring reference samples and for volume/flow-rate checks.

Standards given for the measurement or determination of the sampled volume or of the average flow rate for the sampling period are merely estimates. They are not based on actual data. The error involved in making this determination has been divided into five components. They are: 1) errors in calibrating the rotameter or critical orifice, 2) system leaks between the bubbler and flowmeter, 3) intermittent plugging of lines or critical orifice, loss of power, etc., 4) error in determining the average temperature during the sampling site, and 5) the error in determining the average pressure during the sampling period.

Table 3. METHODS OF MONITORING VARIABLES

Variable	Method of Monitoring
1. Flow-rate calibration	Measurement of volume/flow rate as part of the auditing process.
2. Volume of air sampled	Same as (1) above.
3. Elapsed time between sample collection and analysis	Dates of collection and analysis are taken from the Sample Record Sheet and Operational Data Log Book, respectively, for every sample.
4. Exposure of sample to direct sunlight	Observe operator technique on-site.
5. Entrainment or loss of sample other than by evaporation	Observe operator technique on-site.
6. Purity of chemicals and water	Purity of pararosaniline and water are checked as part of the operating procedure. Other chemicals are purchased as ACS grade.
7. Spectrophotometer calibration	Spectrophotometer calibration is checked with calibrated filters and/or didymium glass when a reference sample cannot be measured within limits.
8. pH of final solution	Measure the pH of the final solution of 1 sample from each site when first starting a quality assurance program and once a month afterwards.
9. Temperature	Temperature should be monitored with a wall thermometer, or if a constant temperature bath is used, a thermometer immersed in the bath.
10. Data processing errors	Data processing checks are performed as a part of the auditing program.

Table 4: SUGGESTED CONTROL LIMITS FOR PARAMETERS AND/OR VARIABLES

Parameter/Variables	Suggested Performance Standards		
	Mean	Standard Deviation	Upper Limit (+3σ)
1. Determination of volume/average flow rate	$\bar{d}_1 = -0.04(\bar{X})$*	$\sigma_1 = 0.025(\bar{X})$	$-0.10(\bar{X})$, $+0.06(\bar{X})$
a) Calibration error	$\bar{d}_a = 0$	$\sigma_a = 0.02(\bar{X})$	
b) System leaks between bubbler or flowmeter	$\bar{d}_b = -0.02(\bar{X})$	$\sigma_b = 0.007(\bar{X})$	
c) Intermittent plugging of lines	$\bar{d}_c = -0.02(\bar{X})$	$\sigma_c = 0.007(\bar{X})$	
d) Error in average temperature of sampling period	$\bar{d}_d = 0$	$\sigma_d = 0.01(\bar{X})$	
e) Error in average pressure of sampling period	$\bar{d}_e = 0$	$\sigma_e = 0.006(\bar{X})$	
Total:			
$\bar{d}_1' = \bar{d}_a + \bar{d}_b + \bar{d}_c + \bar{d}_d + \bar{d}_e$	$\bar{d}_1' = -0.04(\bar{X})$	$\sigma_1' = 0.025(\bar{X})$	
$\sigma_1' = \sqrt{\sigma_a^2 + \sigma_b^2 + \sigma_c^2 + \sigma_d^2 + \sigma_e^2}$			
2. Measurement of reference samples	$\bar{d}_2 = 0$	$\sigma_2 = 0.4$ µg SO_2	± 1.2 µg SO_2

*$\bar{X}$ = mean or average value.

System leaks and intermittent plugging of lines or loss of electrical power would result in a calculated volume of air larger than the volume actually sampled. This in turn would negatively bias the measured concentration. Therefore, $\bar{d}_b$ and $\bar{d}_c$ of Table 4 are shown as negative biases. The other errors are assumed to be normally distributed about a mean value of zero. More accurate estimates of these variables can be made as data from the quality assurance program becomes available.

Combining the means and standard deviations of component errors as

$$\bar{d}_1' = \bar{d}_a + \bar{d}_b + \bar{d}_c + \bar{d}_d + \bar{d}_e$$

and

$$\sigma_1' = \sqrt{\sigma_a^2 + \sigma_b^2 + \sigma_c^2 + \sigma_d^2 + \sigma_e^2}$$

shows that at this level of control the suggested performance standard for measuring the volume/flow-rate is satisfied as is evidenced by

$$\bar{d}_1' = \bar{d}_1$$

and

$$\sigma_1' = \sigma_1.$$

The suggested standard for the measurement of reference samples is the value obtained in a collaborative test of the method (Ref. 6).

PROCEDURES FOR IMPROVING DATA QUALITY

Quality control procedures designed to control or adjust data quality may involve a change in equipment or in operating procedures. Table 5 lists some possible procedures for improving data quality. The applicability or necessity of a procedure for a given monitoring situation will have to be determined from results of the auditing process or special checks performed to identify the important variables. The expected results are given for each procedure in qualitative terms. If quantitative data are available or reasonably good estimates can be made of the expected change in data quality resulting from implementation of each procedure, a graph similar to that in Figure 22, page 105 of the Management Manual can be constructed. The values used in Table 13 and Figure 22 are assumed and were not derived from actual data.

For making cost estimates, a reference system consisting of a sampler equipped with a rotameter and the routine performance of those control checks spelled out in the Operations Manual is assumed.

Table 5. QUALITY CONTROL PROCEDURES OR ACTIONS

Procedure/Action	Description of Action	Expected Results	Costs		
			Equip.	Personnel	Total
A0 Reference Conditions	System using routine procedure as given in the Operations Manual	bias (τ) $=-0.04(\bar{X})$* $\sigma_T = (41)[0.7+0.001(\bar{X})]$	---	---	---
A1 Correct for Temperature	For 24-hour samples obtain from weather station or make on-site measurement of temperature. Estimate an average value for the period and correct sampled volume to 298°K.	Reduces error in calculated sample volume.	15	none	15
A2 Minimize sample shipping and storage time	Minimize time between sample collection and analysis by mailing sample immediately after collection, use special mailing, and analyze as soon after reaching the laboratory.	Reduce the error due the loss of SO_2 with time before analysis.	100	100	200
A3 Temperature control	Use a constant-temperature bath for calibration and analysis.	Reduce variability in the analytical phase due to temperature fluctuations.	250	10	260
A4 Personnel training	Hold a 1-week work shop for operators from all phases of the measurement process once a year.	Reduce operational errors through increased awareness of the pitfalls and increased interest in doing a good job.	none	200	200

*$\bar{X}$ = true concentration of SO_2.

Equipment, manpower requirements, and the continuing cost of labor and supplies are estimated for each procedure. For these estimates technician time was valued at $5 per hour and engineering time at $10 per hour. Equipment life was taken as 5 years. All calculations were based on a sample lot of 100 and an average sampling rate of 60 samples per year per sampling site.

A procedure for selecting the appropriate quality control procedure to insure a desired level of data quality is given below:

(1) Specify the desired performance standard, that is, specify the limits within which you want the deviation between the measured and the true concentration to fall a desired percentage of the time. For example, to measure within $\pm$ 12 percent of the true value, 95 percent of the time, the following performance standards must be satisfied:

$$|\hat{\tau} \pm 2\hat{\sigma}_T| \leq 0.12 \times \mu g\ SO_2/m^3.$$

(2) Determine the system's present performance level from the auditing process, as described on page 101 of the Management Manual, by setting

$$\hat{\tau} = \bar{d}_1 + \bar{d}_2 + \bar{d}_3$$

and

$$\sigma_T = \sqrt{\sigma_1^2 + \sigma_2^2 + \sigma_3^2}\ .$$

If the relationship of (1) above is satisfied, no control procedures are required.

(3) If the desired performance standard is not satisfied, identify the major error components by performing special checks.

(4) Select the quality control procedure(s) which will give the desired improvement in data quality at the lowest cost. Figure 22 on page 105 of the Management Manual illustrates a method for accomplishing this.

The relative position of actions on the graph in Figure 22 will differ for different monitoring networks according to type of equipment being used, available personnel, and local costs. Therefore, each network would need to develop its own graph to aid in selecting the control procedure providing the desired data quality at the lowest cost.

PROCEDURES FOR CHANGING THE AUDITING LEVEL TO GIVE THE DESIRED LEVEL OF CONFIDENCE IN THE REPORTED DATA

The auditing process does not in itself change the quality of the reported data. It does provide a means of assessing the data quality. An increased auditing level increases the confidence in the assessment. It also increases the overall cost of data collection.

Various auditing schemes and levels are discussed on page 82 of the Management Manual. Numerous parameters must be known or assumed in order to arrive at an optimum auditing level. Therefore, only two decision rules with two levels of auditing each will be discussed here.

For conditions as assumed on page 82 of the Management Manual, a study of Figure 20, page 95, gives the following results. These conditions may or may not apply to your operation. They are included here to call attention to a methodology. Local costs must be used for conditions to apply to your operation.

Decision Rule - Accept the Lot as Good If No Defects Are Found (i.e., $d = 0$).

Most Cost Effective Auditing Level - In Figure 20 the two solid lines are applicable to this decision rule, i.e., $d = 0$. The cost curve has a minimum at $n = 7$ or an auditing level of 7 checks out of 100 sampling periods. From the probability curve it is seen that at this auditing level there is a probability of 0.47 of accepting a lot as good when the lot (for $N = 100$) actually has 10 defects. The associated average cost is 240 dollars per lot.

Auditing Level for Low Probability of Accepting Bad Data - Increasing the auditing level to $n = 20$, using the same curve in Figure 20 as above, shows a probability of 0.09 of accepting a lot as good when the lot actually has 10 defects. The average cost associated with this level of auditing is approximately 425 dollars per lot.

Decision Rule - Accept the Lot as Good If No More Than One (1) Defect Is Found (i.e., $d \leq 1$).

Most Cost Effective Auditing Level - From the two dashed curves in Figure 20 it can be seen that the cost curve has a minimum at $n = 14$. At this level of auditing there is a probability of 0.55 of accepting a lot of data as good when it has 10 defects. The average cost per lot is approximately 340 dollars.

Auditing Level for Low Probability of Accepting Bad Data - For an auditing level of $n = 20$ the probability of accepting a lot with 10 percent defects is about 0.36 as read from the $d \leq 1$ probability curve. The average cost per lot is approximately 375 dollars.

It must be realized that the shape of a cost curve is determined by the assumed costs of performing the audit and of reporting bad data. These costs must be determined for individual monitoring situations in order to select optimum auditing levels.

MONITORING STRATEGIES AND COST

Selecting the optimum monitoring strategy in terms of cost and data quality requires a knowledge of the present data quality, major error components, cost of implementing available control procedures, and potential increase in system precision and accuracy.

A methodology for comparing strategies to obtain the desired precision of the data is illustrated in the Management Manual, page 103, Table 5, page 75 lists control procedures with estimated costs of implementation and expected results in terms of which error component(s) are affected by the control. Numerical values of the expected results as given in Table 13, page 106, are estimates and were not derived from actual data.

Three system configurations identified as best strategies in Figure 22, page 105, of the Management Manual are summarized below.

Again, local costs and expected results derived from field data are required to select optimum strategies by this method.

Reference Method (A0)

Description of Method - This refers to a typical sampling operation as described in the Federal Register. Routine operating procedures as given in the Operations Manual are to be followed with special checks performed to identify problem areas when performance standards are not being met. Corrections for delay between collection and analysis and for average temperature are not made. An auditing level of n=7, N=100 is to be carried out for this strategy. This method or strategy is identified as A0 in Table 13 and Figure 22 in the Management Manual.

Costs - Taken as reference or zero cost.

Data Quality - Data quality can be described by

$$(\mu g\ SO_2/m^3)_T = (\mu g\ SO_2/m^3)_m - \hat{\tau} \pm 3\hat{\sigma}_T$$

where $(\mu g\ SO_2/m^3)_T$ = true average concentration of sulfur dioxide, and

$(\mu g\ SO_2/m^3)_m$ = measured average concentration of sulfur dioxide.

Taking the hypothesized values of the bias and standard deviation from Table 13 and using in the above relationship shows that for a true concentration, $(\mu g\ SO_2/m^3)_T$, of 380 $\mu g\ SO_2/m^3$, the measured value, $(\mu g\ SO_2/m^3)_m$, would fall within the following limits

$$308 < (\mu g\ SO_2/m^3)_m < 422$$

approximately 99.7 percent of the time.

Modified Reference Method (A5)

Description of Method - This strategy is identical to the reference method above except that corrections are made for the average temperature for the sampling period (A1) and special personnel training in the form of a yearly workshop.

Costs - The average cost per 100 samples is estimated at 215 dollars above the cost of the reference method (see Figure 22, page 105).

Data Quality - From Table 13, values of bias and standard deviation are seen to be $\hat{\tau} = -0.03$ percent and $\hat{\sigma}_T = 0.035$ percent of the true value. The data quality would be described by

$$(\mu g\ SO_2/m^3)_T = (\mu g\ SO_2/m^3)_m + (0.03 \pm 3 \times 0.035)(\mu g\ SO_2/m^3)_T.$$

For a true concentration 380 $\mu g\ SO_2/m^3$ the measured value would fall within the limits

$$328 < (\mu g\ SO_2/m^3)_m < 409$$

approximately 99.7 percent of the time.

Modified Reference Method Plus Action A2 (A7 = A1 + A2 + A4)

Description of Method - This method is identified as A7 in Figure 22 of the Management Manual. This method is the same as the modified reference method above with the addition of Action A2 which would reduce errors due to loss of SO_2 by minimizing time between collection and analysis.

Costs - Average cost per lot is estimated at 415 dollars above the cost of the reference method.

Data Quality - From Table 13 the data quality would be described by

$$(\mu g\ SO_2/m^3)_T = (\mu g\ SO_2/m^3)_m + (0.01 \pm 0.03)(\mu g\ SO_2/m^3)_T .$$

For a true concentration of 380 $\mu g\ SO_2/m^3$ the measured value would fall within the limits

$$336 < (\mu g\ SO_2/m^3)_m < 416 .$$

Results from these estimated values show that in going from Method A0 to Method A7, the data spread is decreased by about 24 percent and the range is more evenly distributed about the true concentration value.

SECTION IV MANAGEMENT MANUAL

GENERAL

The objectives of a data quality assurance program for the Pararosaniline Method of measuring the concentration of SO_2 in the ambient air were given in Section I. In this part of the document, procedures will be given to assist the manager in making decisions pertaining to data quality based on the checking and auditing procedures described in Sections II and III. These procedures can be employed to:

(1) determine the extent of independent auditing to be performed,

(2) detect when the data quality is inadequate,

(3) assess overall data quality,

(4) relate costs of data quality assurance procedures to a measure of data quality, and to

(5) select from the options available to the manager the alternative(s) which will enable him to meet the data quality goals by the most cost-effective means.

The determination of the extent of auditing is considered in the subsection entitled "Auditing Schemes." Objectives 2 and 3 are discussed in the subsection entitled "Data Quality Assessment," page 96. Finally, Objectives 4 and 5 above are described in the subsection entitled "Data Quality Vs. Cost of Implementing Actions," page 103. The cost data are assumed and a methodology provided. When better cost data become available, improvements can be made in the management decisions.

If the current reference system is providing data quality consistent with that required by the user, there will be no need to alter the physical system or to increase the auditing level. In fact several detailed procedures could be bypassed if continuing satisfactory data quality is implied by the audit. However, if the data quality is not adequate, e.g., either a large bias and/or imprecision exists in the reported data, then (1) increased auditing should be employed, (2) the assignable cause determined, and (3) the system deficiency corrected. The correction can take the form of a change in the operating procedure, e.g., minimize delay between collection and analysis of sample by special mailing; or it may be a change in equipment such as the installation of an improved temperature control system. An increase in the auditing level will increase the confidence in the reported measure of precision/bias and aid in identifying the assignable cause(s) of the large deviations. The level of auditing will be considered in the next subsection.

The audit procedure and the reported results can serve a two-fold purpose. They can be used to (1) screen the data, by lots of say N = 50 or 100, to detect when the data quality may be inadequate, and (2) calculate the bias and precision of the audited measurement and hence estimate the bias/precision of the final reported concentration of SO_2 in the ambient air.

In order to perform (1), suggested standards are provided for use in comparing the audited results with the reported values and a defect is defined in terms of the standards. This approach requires only the reporting of the number of defects in the n auditing checks. In the second method above, it is required to report the measures of bias/precision in the audits. These values are then used in assessing the overall data quality. Approach (1) is suggested as a beginning step even though it will not make maximum use of the data collected in the auditing program. The simplicity of the approach and the explicit definition of a defect will aid in its implementation. After experience has been gained in using the auditing scheme and in reporting and calculating the results, it is recommended that approach (2) be implemented.

It is important that the audit procedure be independent of previously reported results and be a true check of the system under normal operating procedures. Independence can be achieved, for example, by providing a control sample of unknown concentration of SO_2 to the operator and requesting that he measure and report the concentration of the sample. To insure that the check is made under normal operating procedures, it is required that the audit be performed without any special check of the system prior to the audit other than that usually performed during each sampling period.

AUDITING SCHEMES

Auditing a measurement process costs time and money. On the other hand, reporting poor quality data can also be very costly. For example, the reported data might be used to determine a relationship between health damage and concentrations of certain pollutants. If poor quality data are reported, it is possible that invalid inferences or standards derived from the data will cost many dollars. These implications may be unknown to the manager until some report is provided to him referencing his data; hence, the importance of reporting the precision and bias with the data.

Considering the cost of reporting poor quality data, it is desirable to perform the necessary audits to assess the data quality and to invalidate unsatisfactory data with high probability. On the other hand, if the data quality is satisfactory, an auditing scheme will only increase the data measurement and processing cost. An appropriate tradeoff or balance of these costs must be sought. These costs are discussed under Cost Relationships.

Now consider the implication of an auditing scheme to determine or judge the quality of the reported data in terms of an acceptance sampling scheme. Let the data be assembled into homogeneous lots of N = 50 or 100 sampling periods. Suppose that n periods are sampled in the manner suggested in Section III. That is, the N = 50 or 100 sampling periods are subdivided into equal time intervals (as nearly equal as possible); then one day is selected at random during each interval. Figure 17 gives a diagram of the data flow, sampling, and decision making process for an auditing level of n = 7.

Statistics of Various Auditing Schemes

Suppose that the lot size is N = 100 periods (days), that n = 7 periods are selected at random, and that there are 5% defectives in the 100, or 5 defectives. The probability that the sample of 7 contains 0, 1, ..., 5 defectives is given by the following.

$$p(0 \text{ defectives}) = \frac{\binom{5}{0}\binom{95}{7}}{\binom{100}{7}} \quad *,$$

and for d defectives

$$p(d \text{ defectives}) = \frac{\binom{5}{d}\binom{95}{7-9}}{\binom{100}{7}}, \quad d \leq 5.$$

The values are tabulated below for d = 0, 1, ..., 6 and for the two data quality levels.

Table 6. P(d defectives)

	Data Quality	
d	D=5% Defectives	D=15% Defectives
0	0.6903	0.3083
1	0.2715	0.4098
2	0.0362	0.2152
3	0.0020	0.0576
4	0.00004	0.0084
5	≈ 0	0.0007
6	$= 0$	≈ 0

* $\frac{\binom{5}{0}\binom{95}{7}}{\binom{100}{7}} = \frac{\frac{5!}{0!5!}\ \frac{95!}{7!88!}}{\left(\frac{100!}{7!93!}\right)} = \frac{95 \cdot 94 \cdots 89}{100 \cdot 99 \cdots 94} = 0.6903.$

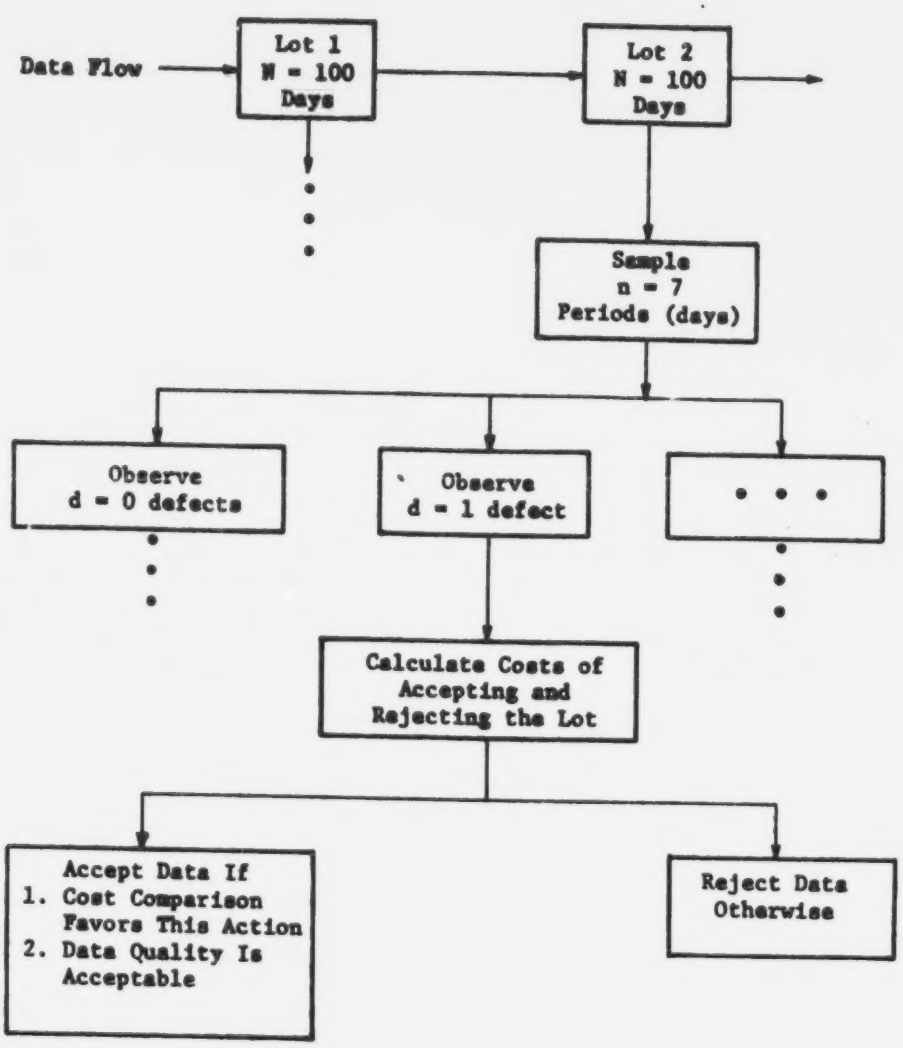

Figure 17: Data Flow Diagram for Auditing Scheme

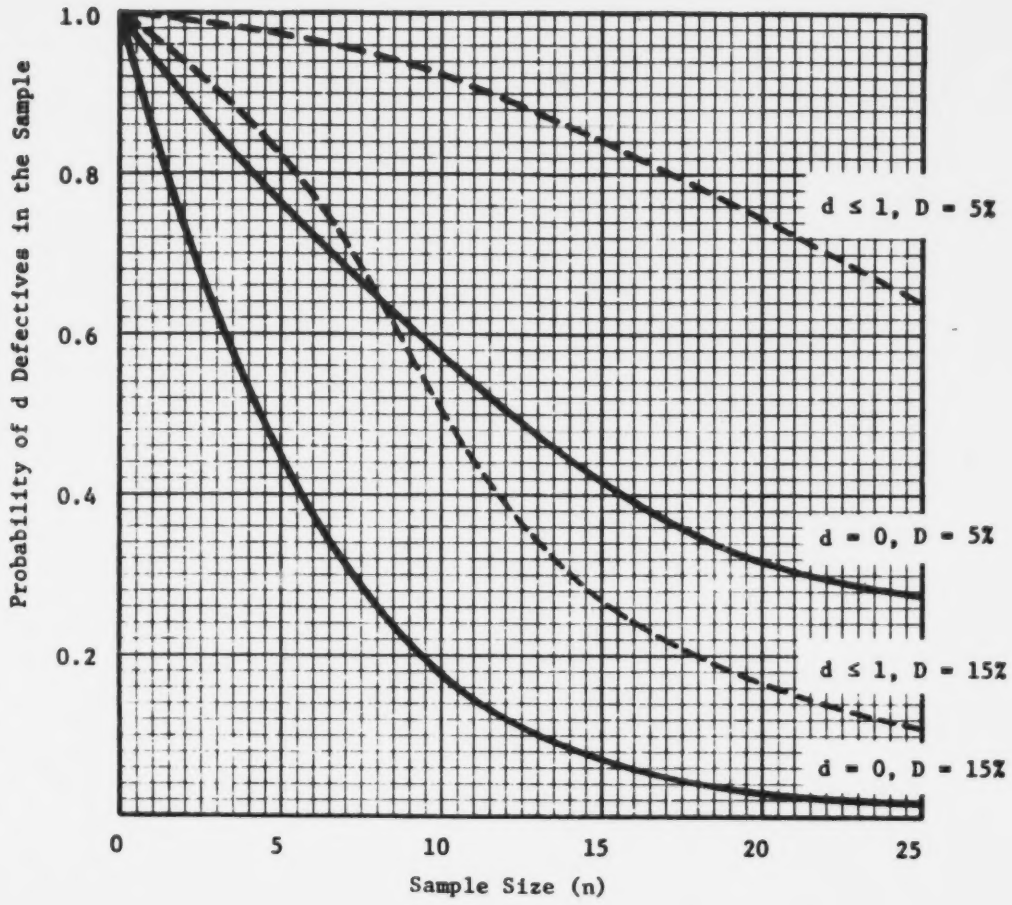

Figure 18A: Probability of d Defectives in the Sample If the Lot (N = 100) Contains D% Defectives

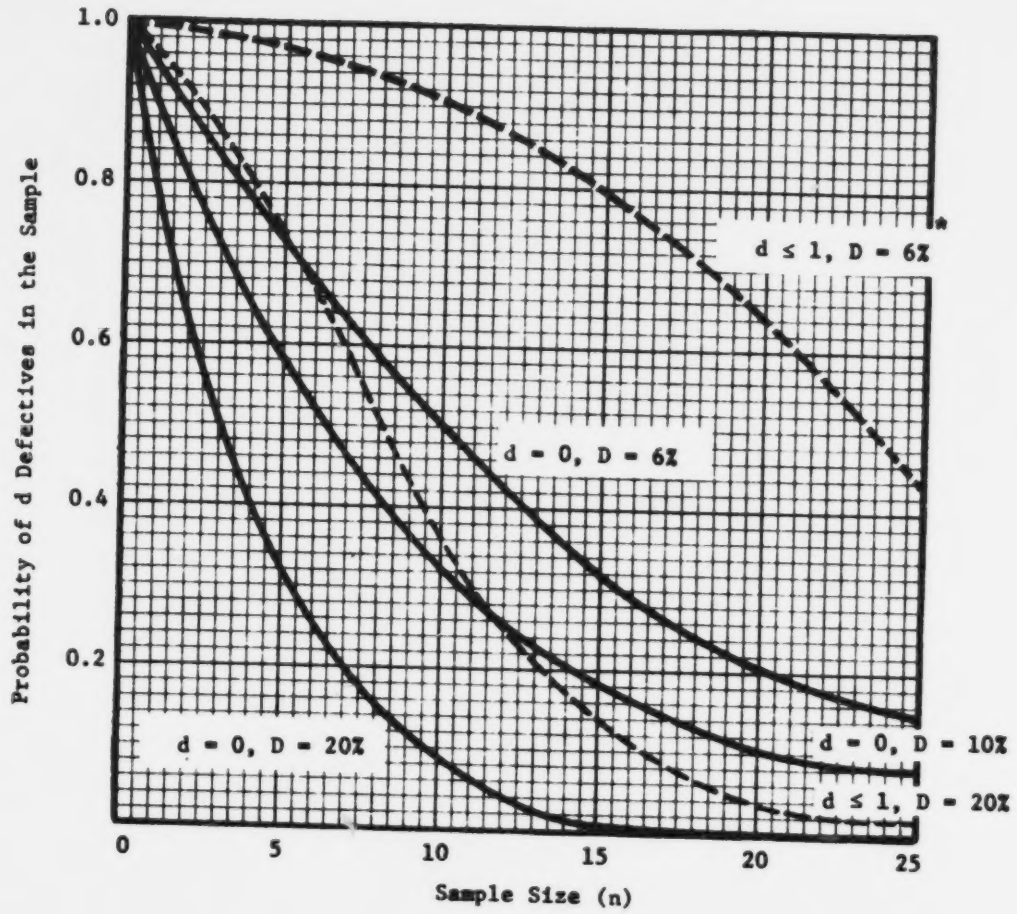

Figure 18B: **Probability of d Defectives in the Sample If the Lot (N = 50) Contains D% Defectives.**

*This graph is for a lot size of N = 50. Only whole numbers of defectives are physically possible; therefore, even values of D (i.e., 6, 10, and 20 percent) are given rather than the odd values of 5 and 15 percent as given in **Figure** 18A.

Figure 18A gives the probabilities of d = 0 and d $\leq$ 1 defectives as a function of sample size. The probability is given for lot size N = 100, D = 5 and 15% defectives, for sample sizes (auditing levels) from 1 to 25. For example, if n = 10 measurements are audited and D = 5% defectives, the probability of d = 0 defectives is 0.58. Figure 18B gives the probabilities for lot size N = 50, for D = 6, 10, and 20% defectives, and for d = 0 and d $\leq$ 1. These curves will be used in calculating the cost relationships.

Selecting the Auditing Level

One consideration in determining an auditing level n used in assessing the data quality is to calculate the value of n which for a prescribed level of confidence will imply that the percent of defectives in the lot is less than 10 percent, say, if zero defectives are observed in the sample.* Figures 19A and 19B give the percentage of good measurements in the lot sampled for several levels of confidence, 50, 60, 80, 90, and 95%. The curves in Figure 19A assume that 0 defectives are observed in the sample, and those in Figure 19B that 1 defective is observed in the sample. The solid curves on the figures are based on a lot size of N = 100; two dashed curves are shown in Figure 19A for N = 50; the differences between the corresponding curves are small for the range of sample sizes considered.

For example, for zero defectives in a sample of 7 from a lot of N = 100, one is 50% confident that there are less than 10% defective measurements among the 100 reported values. For zero defectives in a sample of 15 from N = 100, one is 80% confident that there are less than 10% defective measurements. Several such values were obtained from Figure 19A and placed in Table 7 below for convenient reference.

Table 7. REQUIRED AUDITING LEVELS n FOR LOT SIZE N = 100 ASSUMING ZERO DEFECTIVES

Confidence Level	D = 10%	15%	20%
50%	7	<5	<5
60%	9	6	<5
80%	15	10	8
90%	20	15	11
95%	$\approx$ 25	18	13

*Obviously, the definition of defective need not always be the same and must be learly stated each time. The definitions employed herein are based on results given in the collaborative test report (Ref. 6).

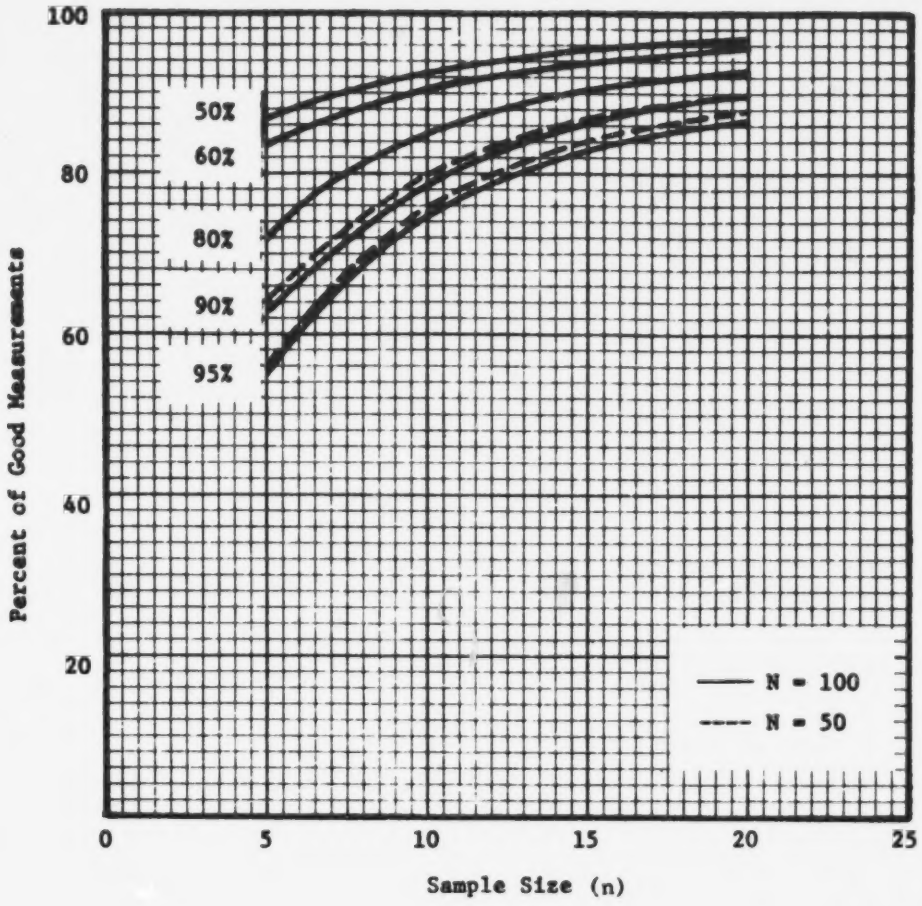

Figure 19A: Percentage of Good Measurements Vs. Sample Size for No Defectives and Indicated Confidence Level

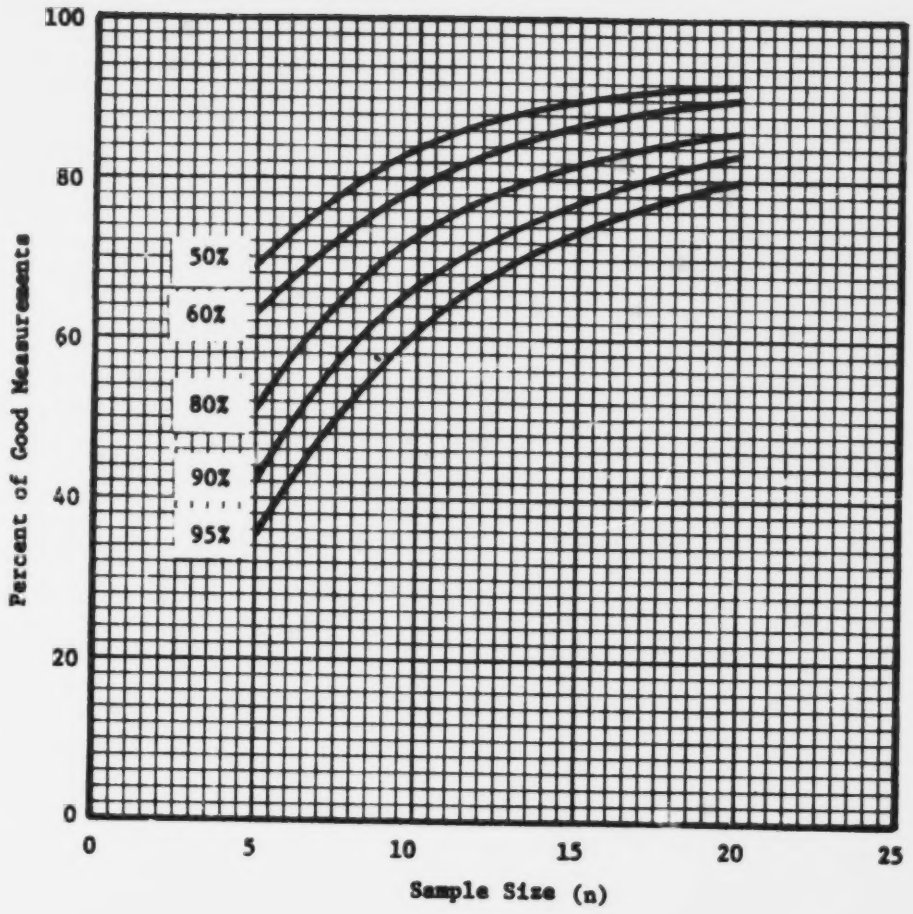

Figure 19B: Percentage of Good Measurements Vs. Sample Size for 1 Defective Observed and Indicated Confidence Level

Lot Size = 100

Cost Relationships

The auditing scheme can be translated into costs using the costs of auditing, rejecting good data, and accepting poor quality data. These costs may be very different in different geographic locations. Therefore, purely for purposes of illustrating a method, the cost of auditing is assumed to be directly proportional to the auditing level. For n = 7 it is assumed to be $155 per lot of 100. The cost of rejecting good quality data is assumed to be $600 for a lot of N = 100. The cost of reporting poor quality data is taken to be $800. To repeat, these costs given in Table 8 are assumed for the purpose of illustrating a methodology of relating auditing costs to data quality. Meaningful results can only be obtained by using correct local information.

Table 8. COSTS VS. DATA QUALITY

	Data Quality	
	"Good"	"Bad"
	D ≤ 10%	D > 10%
	Incorrect Decision	Correct Decision
Reject Lot of Data	Lose cost of performing* audit plus cost of rejecting good quality data. (-$600 - $155)	Lose cost of performing audit, save cost of not permitting poor quality data to be reported. ($400 - $155)
	Correct Decision	Incorrect Decision
Accept Lot of Data	Lose cost of performing audit. (-$155)	Lose cost of performing audit plus cost of declaring poor quality data valid. (-$800 - $155)

Suppose that 50 percent of the lots have more than 10 percent defectives and 50 percent have less than 10 percent defectives. (The percentage of defective lots can be varied as will be described in the final report under the contract.) For simplicity of calculation, it is further assumed that the good lots have exactly 5 percent defectives and the poor quality lots have 15 percent defectives.

* Cost of performing audit varies with the sample size; it is assumed to be $155 for n = 7 audits per N = 100 lot size.

Suppose that n = 7 measurements out of a lot of N = 100 have been audited and none found to be defective. Furthermore, consider the two possible decisions of rejecting the lot and accepting the lot and the relative costs of each. These results are given in Tables 9A and 9B.

Table 9A. COSTS IF 0 DEFECTIVES ARE OBSERVED AND THE LOT IS REJECTED

		Correct Decision	Incorrect Decision	Net Value ($)
Reject Lot	D = 5%	---	$p_1 = 0.69$ $C_1 = -600 - 155$	$p_1C_1 = -\$521$
	D = 15%	$p_2 = 0.31$ $C_2 = 400 - 155$	---	$p_2C_2 = \$76$

Cost = $p_1C_1 + p_2C_2 = -\$445$

Table 9B. COSTS IF 0 DEFECTIVES ARE OBSERVED AND THE LOT IS ACCEPTED

		Correct Decision	Incorrect Decision	Net Value ($)
Accept Lot	D = 5%	$p_1 = 0.69$ $C_3 = -155$	--- ---	$p_1C_3 = -\$107$
	D = 15%	---	$p_2 = 0.31$ $C_4 = -800 - 155$	$p_2C_4 = -\$296$

Cost = $p_1C_3 + p_2C_4 = -\$403$

The value $p_1(p_2)$ in the above table is the probability that the lot is 5% (15%) defective given that 0 defectives have been observed. For example,

$$p_1 = \frac{\left(\begin{array}{c}\text{probability that the lot is 5\% defective} \\ \underline{\text{and}}\ 0 \text{ defectives are observed}\end{array}\right)}{p\left(\begin{array}{c}\text{lot is 5\% defective } \underline{\text{and}} \\ 0 \text{ defectives observed}\end{array}\right) + p\left(\begin{array}{c}\text{lot is 15\% defective } \underline{\text{and}} \\ 0 \text{ defectives observed}\end{array}\right)}$$

$$= \frac{0.5(0.69)}{0.5(0.69) + 0.5(0.31)} = 0.69 .$$

$$p_2 = \frac{\left(\begin{array}{c}\text{probability that the lot is 15\% defective} \\ \underline{\text{and}}\ 0 \text{ defectives are observed}\end{array}\right)}{p\left(\begin{array}{c}\text{lot is 5\% defective } \underline{\text{and}} \\ 0 \text{ defectives observed}\end{array}\right) + p\left(\begin{array}{c}\text{lot is 15\% defective } \underline{\text{and}} \\ 0 \text{ defectives observed}\end{array}\right)}$$

$$= \frac{0.5(0.31)}{0.5(0.31) + 0.5(0.69)} = 0.31 .$$

It was assumed that the probability that the lot is 5% defective is 0.5. The probability of observing zero defectives, given the lot quality is 5% or 15%, can be read from the graph of Figure 18A.

A similar table can be constructed for 1, 2, ..., defectives and the net costs determined. The net costs are tabulated in Table 10 for 1, 2, and 3 defectives. The resulting costs indicate that the decision preferred from a purely monetary viewpoint is to accept the lot if 0 defectives are observed and to reject it otherwise. The decision cannot be made on this basis alone. The details of the audit scheme also affect the confidence which can be placed in the data qualification; consideration must be given to that aspect as well as to cost.

Table 10. COSTS IN DOLLARS

Decision	d = number of defectives			
	0	1	2	3
Reject Lot	-445	-155	+101	+207
Accept Lot	-403	-635	-839	-928

Cost Versus Audit Level

After the decision criteria have been selected, an average cost can be calculated. Based on the results of Table 10, the decision criterion is to accept the lot if d = 0 defectives are observed and to reject the lot if d = 1 or more defectives are observed. All the assumptions of the previous section are retained. The auditing level is later varied to obtain the data in Figure 20, page 95.

One example calculation is given below and summarized in Table 11. The four cells of Table 11 consider all the possible situations which can occur, i.e., the lots may be bad or good and the decision can be to either accept or reject the lot based on the rule indicated by Table 10. The costs are exactly as indicated in Tables 9A and 9B. The probabilities are computed as follows.

q_1 = (prob. that the lot is 5% defective and 1 or more defects are obtained in the sample)

= (prob. that the lot is 5% defective)(prob. 1 or more defectives are obtained in the sample given the lot is 5% defective)

= 0.5 (0.31) = 0.155

Similarly q_2, q_3, and q_4 in Table 11 are obtained as indicated below.

q_2 = 0.5 (0.69) = 0.345

q_3 = 0.5 (0.69) = 0.345

q_4 = 0.5 (0.31) = 0.155 .

The sum of all the q's must be unity as all possibilities are considered. The value of 0.5 in each equation is the assumed proportion of good lots (or poor quality lots). The values of 0.31 and 0.69 are the conditional probabilities that given the quality of the lot, either d = 0 or d = 1 or more defectives are observed in the sample. Further details of the computation are given in the final report of this contract.

Table 11. OVERALL AVERAGE COSTS FOR ONE ACCEPTANCE - REJECTION SCHEME

Decision	Good Lots D = 5%	Bad Lots D = 15%	
Reject any lot of data if 1 or more defects are found.	q_1 = 0.155 C_1 = -\$755	q_2 = 0.345 C_2 = \$245	$q_1C_1 + q_2C_2$ = -\$ 32
Accept any lot of data if 0 defects are found.	q_3 = 0.345 C_3 = -\$155	q_4 = 0.155 C_4 = -\$955	$q_3C_3 + q_4C_4$ = -\$202
			Average Cost = -\$234

In order to interpret the concept of average cost, consider a large number of data lots coming through the system; a decision will be made on each lot in accordance with the above, and a resulting cost of the decision will be determined. For a given lot, the cost may be any one of the four costs, and the proportion of lots with each cost is given by the q's. Hence the overall average cost is given by the sum of the product of q's by the corresponding C's.

In order to relate the average cost as given in Table 11 to the costs given in Table 10, it is necessary to weight the costs in Table 10 by the relative frequency of occurrence of each observed number of defectives, i.e., prob(d). This calculation is made below.

No. of Defectives	Decision Rule	Costs ($) from Table 10	Prob(d)	Cost × Prob(d)
d = 0	Accept	- 403	0.50	-$201.5
1	Reject	- 155	0.34	- 52.7
2	Reject	101	0.1255	12.6
3	Reject	207	0.030	6.2
4	Reject	244	0.0042	1.0
		Totals	0.9997	-$234.4

Thus the value -$234 is the average cost of Table 11 and the weighted average of the costs of Table 10. The weights, Prob(d), are obtained as follows:

Prob(d=0) = Prob(lot is good and d=0 defectives are observed)

+ Prob(lot is poor quality and d=0 defectives are observed)

= 0.5(0.69) + 0.5(0.31) = 0.50 .

This is the proportion of all lots which will have exactly 0 defectives under the assumptions stated. For d = 1, 2, 3, and 4, the values of the probabilities in parentheses above can be read from Table 6.

Based on the stated assumptions, the average cost was determined for several auditing levels as indicated in Table 11. These costs are given in Figure 20. One observes from this figure that n = 7 is cost effective given that one accepts it only if zero defectives are observed. (See curve for d = 0.)

If the lots are accepted if either 0 or 1 defectives are observed, then referring to the curve $d \leq 1$, the best sampling level is n = 14. The curve of probability of $d = 0$ ($d \leq 1$) defectives in a sample of n from a lot of N = 100 measurements, given that there are 10% defectives in the lot, is also given on the same figure.

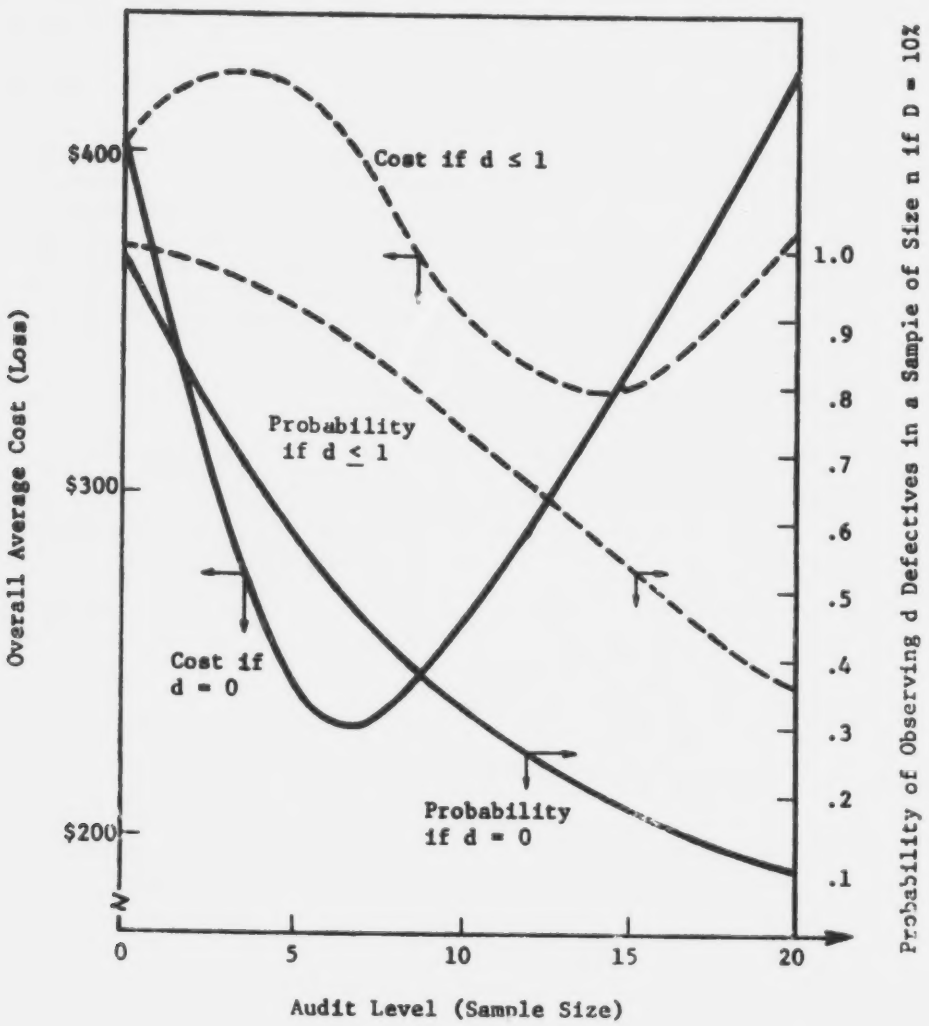

Figure 20: Average Cost Vs. Audit Level
(Lot Size N = 100)

Another alternative is to accept all data without performing an audit. Assuming that one-half (50%) of the lots contain more than 10% defectives, the average cost on a per lot basis would be 0.5(-$800) = -$400. This, however, would preclude qualification of the data. Regardless of cost, it would be an unacceptable alternative.

DATA QUALITY ASSESSMENT

In this section, approach 2 is considered; that is, the precisions and biases of the individual measurements and operational procedures are estimated. These results are then used to make an assessment of the data quality. Although it is theoretically possible to make an overall assessment, e.g., similar to what was done in the collaborative test program, this is not a practical possibility due to the high cost. The following audit scheme is one which is considered reasonable in both cost and effort.

Assessment of Individual Measurements

Assume for convenience that an auditing period consists of N = 100 days (or sampling periods). Subdivide the auditing period into n equal or nearly equal periods. Make one audit during each period and compute the deviations (differences) between the audit values and the stated values (or previously determined values as measured by the operator) as indicated in the Supervision Manual. For example, if seven audits (n = 7) are to be performed over 100 sampling periods (N = 100), the 100 periods can be subdivided into 7 intervals (6 with 14 periods and 1 with 16 periods). Select one day at random within each interval and perform the suggested audits. The operator should not be aware of when the checks are to be performed.

For sites operating every sixth day, a minimum of three audits per quarter is recommended. Samples from individual sites can be grouped into logical lots, e.g., all sites for which a single operator is responsible, to form data lots of at least 50 samples. This approach insures that the audit level will exceed n = 7 for the combined sites and resulting data.

In order to assess the data quality using measures of bias/precision, the checks are to be combined for the selected auditing period, and the mean difference or bias and the standard deviation of the differences are to be computed as indicated below.

The formulas for average bias and the estimated standard deviations are the standard ones given in statistical texts (e.g., see Ref. 9). The level of sampling or auditing, n, will be considered as a parameter to be selected by the manager to assess the quality of data as required.

(1) Flow Rate/Volume Check

$$\text{Bias} = \bar{d}_1 = \frac{\sum_{j=1}^{n} d_{1j}}{n},$$

where

d_{1j} = percent difference in the average flow rate using the three-point and two-point approximation, or if suitable instrumentation can be obtained to measure the integrated volume, the percent difference in volumes computed by the auditing equipment and by regular means using the initial and final flow rates (see page 46).

$$\text{Standard Deviation} = s_1 = \sqrt{\frac{3}{5} \frac{\Sigma(d_{1j} - \bar{d}_1)^2}{n - 1}}^{*},$$

where

$\bar{d}_1$ = the average bias, and

s_1 = the estimated standard deviation of the average of the initial and final flow rates.

(2) Reference Sample Check

Results of the measurement of reference samples are reported as $d = (\mu gSO_2)_m - (\mu gSO_2)_c$ as directed on page 51. Compute the percentage difference by

$$d_{2j} = \frac{(\mu gSO_2)_m - (\mu gSO_2)_c}{(\mu gSO_2)_c} \times 100.$$

Compute the bias and standard deviation by

$$\text{Bias} = \bar{d}_2 = \frac{\sum_{j=1}^{n} d_{2j}}{n},$$

where

d_{2j} = percent difference in the measured and known value of the j^{th} control sample.

---

*The factor $\frac{3}{5}$ is inserted in the expression for s_1 to account for the fact that the variance of d_{1j} is 5/3 times the variance of the average flow rate as determined by the average of the initial and final flow rates. It is assumed that the individual flow-rate measurements have the same variances.

$$\text{Standard Deviation} = s_2 = \sqrt{\frac{\Sigma(d_{2j} - \bar{d}_2)^2}{n - 1}} ,$$

where

$\bar{d}_2$ = the average bias, and

s_2 = the estimated standard deviation of the differences in the measured and known concentration of control samples.

(3) Data Processing Check

$$\text{Bias} = \bar{d}_3 = \frac{\sum_{j=1}^{n} d_{3j}}{n} ,$$

where

d_{3j} = percent deviation of the concentration of SO_2 as calculated by the operator and by that calculated from the audit.

$$\text{Standard Deviation} = s_3 = \sqrt{\frac{\Sigma(d_{3j} - \bar{d}_3)^2}{n - 1}} .$$

where

$\bar{d}_3$ = the average bias, and

s_3 = the estimated standard deviation of the data processing errors.

Individual checks on the standard deviations of the three audits can be made by computing the ratio of the estimated standard deviation, s_j, to the corresponding suggested performance standard, σ_j, given in Table 12. If this ratio exceeds values given in Table 12 for any one of the two audits, it would indicate that the source of trouble may be assigned to that particular aspect of the measurement process. Critical values of this ratio are given in Figure 21 as a function of sample size and two levels of confidence. Having assessed the general problem area, one then needs to perform the appropriate quality control checks to determine the specific causes of the large deviations.

Table 12. CRITICAL VALUES OF s_i/σ_i

Level of Confidence	Statistic	Audit Level				
		n=5	n=10	n=15	n=20	n=25
90%	s_i/σ_i	1.40	1.29	1.23	1.20	1.18
95%	s_i/σ_i	1.54	1.37	1.30	1.26	1.23

s_i = estimated standard deviation

σ_i = hypothesized or suggested standard deviation.

Audit	Suggested Performance Standard
Flow Rate (or Volume) Check	$\sigma_1 = 0.025 \times \overline{\mu g\ SO_2/m^3}$
Control Sample	$\sigma_2 = 0.4\ \mu g\ SO_2$*
Data Processing Check	$\sigma_3 = 0.03 \times \overline{\mu g\ SO_2/m^3}$

*σ_2 is based on information in Ref. 6 it must be converted to a percent for use in the following subsection.

Overall Assessment of Data Quality

The values of $\bar{d}_1$, $\bar{d}_2$, $\bar{d}_3$, s_1, s_2 and s_3 above measure the bias and variation of the reported data for the three selected audits. As stated previously, these three audits do not completely evaluate the measurement process. A partial or limited evaluation is used because of the high cost of a complete evaluation and the unavailability of a cheap and reliable method of generating test atmospheres of specified concentration with high precision from one laboratory to another. These three measures can be combined to estimate the bias and standard deviation of that aspect of the process which is audited. The standard deviation of the measured concentration of SO_2 is calculated by using the individual standard deviations expressed in percent error as

$$\hat{\sigma}_T \text{ (in \%)} = \sqrt{s_1^2 + s_2^2 + s_3^2}$$

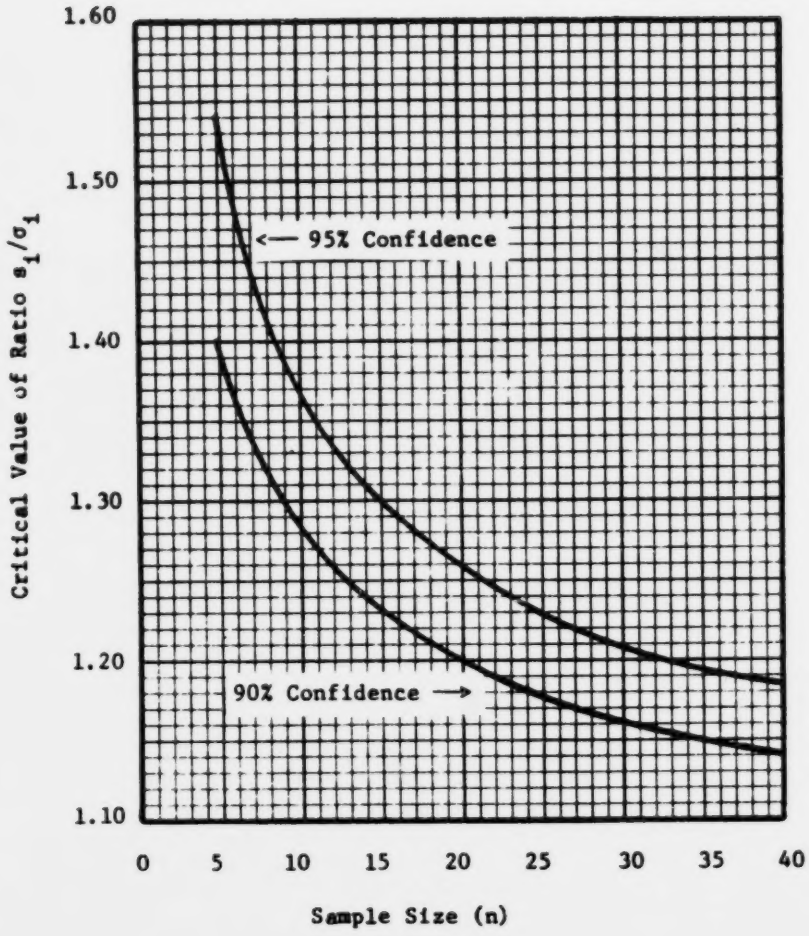

Figure 21: Critical Values of Ratio s_1/σ_1 Vs. n

Using the estimated coefficient of variation $\hat{\sigma}_T$ (in percent) and the mean concentration of SO_2 one obtains

$$\hat{\sigma}_T \ (\mu g \ SO_2/m^3) = \hat{\sigma}_T \ (\text{in } \%) \cdot \overline{\mu g \ SO_2/m^3} \ ,$$

an estimated standard deviation of the part of the measurement process which is audited.

Development of a Model - The final report of this project discusses a modeling technique for combining the errors of observation and/or the variation of environmental effects to make an overall assessment and the assumptions required in the use of the technique. The basis for the model is the equation for the measured concentration of SO_2, i.e.,

$$(1) \qquad \mu g \ SO_2/m^3 = \frac{(A - A_o) \ 10^3 \ B_s}{V_R} \times D$$

where the individual parameters are defined in the Federal Register and included in the Appendix for convenience. Each of the variables in equation (1) is further modeled in terms of the errors/variations in the method of measurement, operator, and environmental effects as described in the final report on this project. When the model is completely formulated, an analysis of the mean concentration (or bias) and its estimated standard deviation can be performed. For the assumed variations in each of the variables the bias was negative and about 5%, the standard deviation was about 10%, both based on 400 $\mu g/m^3$ as the true concentration. The bias estimate can be obtained by substituting into the computational formula for $\mu g \ SO_2/m^3$ the averages adjusted for the measured biases and thus estimating the bias on the reported concentration. This calculated bias is denoted by $\hat{\tau}$. The composite of these two measures into a mean square error (MSE), i.e.,

$$\text{MSE} = \sqrt{(\text{Bias effect})^2 + (\text{Std. Dev.})^2}$$

$$= 11.2\%$$

yields a value which might be compared to reproducibility of results obtained in the field. It must be emphasized that to obtain these results, estimates of the standard deviations of results were obtained from Ref. 6 when available and by statistical or engineering judgment otherwise.

The estimates of $\hat{\tau}$ and $\hat{\sigma}$ obtained from the model can be used in reporting the bias and precision as suggested by the following. The true concentration of SO_2 should fall in the following interval, where $(\mu g\ SO_2/m^3)_m$ is the measured concentration,

$$(\mu g\ SO_2/m^3)_m - \hat{\tau} \pm 2\hat{\sigma}_T,$$

approximately 95% of the time, or within the interval

$$(\mu g\ SO_2/m^3)_m - \hat{\tau} \pm 3\hat{\sigma}_T,$$

approximately 99.7% of the time. When computed from audit data, the coefficients of $\hat{\sigma}_T$ are actually dependent on the number of audits conducted. If n is large, say about 25 or larger, the value 2 (or 3) is appropriate.

In reporting the data quality, the bias, overall standard deviation, and auditing level should be reported in an ideal situation (see the section entitled "Data Presentation" for further discussion). More restricted information following approach 1 is suggested in the Supervision Manual as a minimal reporting procedure.

If the overall reported precisions/biases of the data meet or satisfy the requirements of the user of the data, then a reduced auditing level may be employed; on the other hand, if the data quality is not adequate, assignable causes of large deviations should be determined and appropriate action taken to correct the deficiencies. This determination may require increased checking or auditing of the measurement process as well as the performance of certain quality control checks, e.g., monitoring of temperature variations over the 24-hour sampling period.

Identification of the Important Parameters - The next step in the modeling process was to use the model to identify the critical parameters, i.e., those parameters which may cause the greatest variation in the measured concentration, SO_2, if their variation is of the order of magnitude assumed in the analysis. Two types of analyses were employed to determine the critical parameters and the combined effect of all the parameters on the variation in the measured concentration of $\mu g\ SO_2/m^3$.

The first type was a sensitivity or ruggedness analysis which identified and ranked the critical parameters, made certain checks on the adequate of a linear approximation to the developed model, and estimated the variation (as measured by the standard deviation) of SO_2 through the use of a linear approximation. This latter technique was a straightforward

application of error analysis. The second analysis procedure was a Monte Carlo simulation in which each of the parameters was assigned a distribution of values: for example, the slope of the calibration curve was assumed to be normally distributed with given mean and standard deviation. This simulation analysis provided a listing of the simulated values of concentration in ascending order and calculated the mean and standard deviation and other pertinent characteristics of this distribution. These analyses are described in further detail in the final report of this contract.

Results from the above analyses may not be valid for one specific situation, but should be a reasonably good evaluation of average precision and accuracy obtainable over a large population of measurements. The results indicate that if the operating procedures recommended in the Operations Manual were adhered to, the measured data would have a mean value negatively biased from the true value of concentration (about) 5%, and a standard deviation of approximately 10% of the mean value ($\hat{\sigma}_T = 0.10 \times \overline{\mu g\ SO_2}/m^3$) for a true concentration of 400 $\mu g\ SO_2/m^3$.

Values derived from the above analyses were used to arrive at suggested performance standards, and to a certain extent, for suggested control limits given for certain checks in the Operations Manual.

The standard deviation of SO_2 is a measure of the precision or variation of the reported values of SO_2 as estimated by the model. It is to be noted that this measure depends on the estimated standard deviations of each of the variables and on the coefficients in the model, which are dependent on the form of the model. These values can be checked using the biases and standard deviations computed from actual field data.

DATA QUALITY VERSUS COST OF IMPLEMENTING ACTIONS

The discussion and methodology given in a previous section were concerned with the auditing scheme (i.e., level of audit or sample size, costs associated with the data quality, etc.). Increasing the level of audit of the measurement process does not by itself change the quality of the data, but it does increase the information about the quality of the reported data. Hence, fewer good lots will be rejected and more poor quality data will be rejected. If the results of the audit imply that certain process measurement variables or operational procedures are major contributors to the total error or variation in the reported concentration of SO_2, then alternative strategies for reducing these variations need to be investigated. This section illustrates a methodology for comparing the strategies to obtain the desired precision of the data. In practice it would be necessary to experiment with one or more strategies, to determine the potential increase in precision, and to relate the precisions to the relative costs as indicated herein. Several strategies are considered, but only a few of the least costly ones would be acceptable, as illustrated in Figure 22. The assumed values of the standard deviations and biases for each strategy and audit are not based on actual data, except for the reference method. In this case values were taken from the results of the collaborative test program (Ref. 6).

Several alternative actions or strategies can be taken to increase the precision of the reported data. For example, if the temperature variations are large, the measurement methods may vary and, cause variation in $\mu g\ SO_2/m^3$. Under these conditions additional control equipment for temperature variation can reduce the variation of the measured responses by calculated amounts and thus reduce the error of the reported concentrations. In this manner, the cost of the added controls can be related to the data quality as measured by the estimated bias/precision of the reported results.

In order to determine a cost efficient procedure, it is necessary to estimate the variance for each source of error (or variation) for each strategy and then to select the strategy or combination of strategies which yields the desired precision with minimum cost. These calculations are summarized in Table 13 with assumed costs of equipment and control procedures. The various strategies are given in Table 5 of Section III.

Suppose that it is desired to make a statement that the true SO_2 concentration is within 12% of the measured concentration (for simplicity of discussion all calculations were made at a true concentration of $380\ \mu g/m^3$) with approximately 95 percent confidence. Minimal cost control equipment and checking procedures are to be employed to attain this desired precision. Examining the graph in Figure 22 of cost versus precision, one observes that A2 is the least costly strategy that meets the required goal of $2MSE \leq 12$ or $MSE \leq 6$ percent. The mean square error ($MSE = \sqrt{\sigma^2 + \tau^2}$) is used in this analysis as a means of combining the bias (τ) and standard deviation (σ) to obtain a single measure of the overall dispersion of the data. The assumed values of the MSE's of the measured concentrations of SO_2 for the alternative courses of action are given in Table 13. The costs for the various alternatives are given in Table 5 of Section III and in Table 13.

Suppose that it is desired that MSE be less than 4% and that the cost of reporting poor quality data increases rapidly for MSE greater than 4%, then strategy A6 = (A2 + A4) appears best because it meets the goal of MSE being less than 4%, its costs of implementation is \$400/100 samples. However, strategy A5 costs \$215 to implement and results in a cost of about \$40 for reporting poor quality data; an overall cost of \$255 compared to \$400 for A6. Based on the assumed values A5 would be best. This example demonstrates the need for the manager to obtain estimates of the improvements in data quality which can be attained through various actions. This assumption is illustrated by the cost curve given by the solid line in Figure 22. For any alternative strategy, the cost of reporting poor quality data is given by the ordinate of this curve corresponding to the strategy.

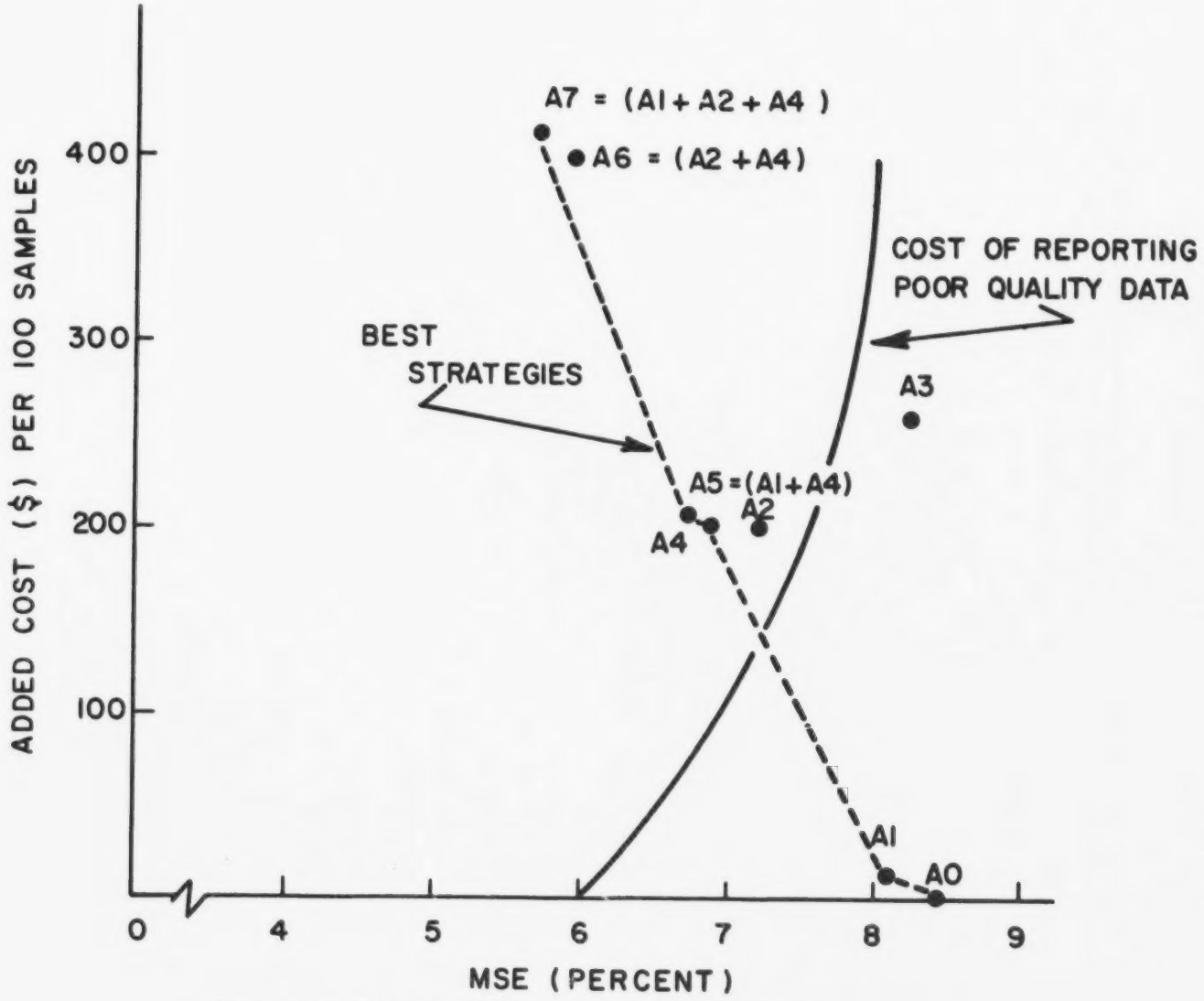

Figure 22: Added Cost ($) vs. MSE (%) for Alternative Strategies

Table 13. ASSUMED STANDARD DEVIATIONS FOR ALTERNATIVE STRATEGIES[1/]

		A0	A1	A2	A3	A4	A5[2/]	A6[2/]	A7[2/]
1. Flow rate	$\bar{d}_1$	-4	-4	-4	-4	-3	-3	-1	-1
	σ_1	σ_1	$0.6\sigma_1$	σ_1	σ_1	$0.7\sigma_1$	$0.42\sigma_1$	$0.7\sigma_1$	$0.42\sigma_1$
2. Control sample	$\bar{d}_2$	0	0	0	0	0	0	0	0
	σ_2	σ_2	σ_2	$0.7\sigma_2$	$0.8\sigma_2$	$0.8\sigma_2$	$0.8\sigma_2$	$0.56\sigma_2$	$0.56\sigma_2$
3. Data processing	$\bar{d}_3$	0	0	0	0	0	0	0	0
	σ_3	σ_3	σ_3	σ_3	σ_3	$0.7\sigma_3$	$0.7\sigma_3$	$0.7\sigma_3$	$0.7\sigma_3$
σ_T (%)		5.0	4.7	5.1	4.7	3.8	3.5	3.8	3.5
Negative bias = -(%)		4	4	1	4	3	3	1	1
MSE(%)[4/]		6.5	6.2	5.2	6.2	4.8	4.6	3.9	3.7
Added cost ($) per 100 samples		0	15	200	260	200	215	400	415

[1/] σ_2 = 0.4 µg SO_2, for a 24-hour sample at 380 µg SO_2/m^3 where 0.32 m^3 of air is sampled, σ_2 = 0.4 μ_g SO_2 is equivalent to a standard deviation of 3.3%.

σ_1 and σ_3 are assumed to be 2.5% and 3% respectively of the average or mean value, $\bar{X}$ = 380 µg SO_2/m^3.

$\bar{d}_1$ is also expressed as the bias in % of the mean concentration, $\bar{X}$ = 380 µg SO_2/m^3.

[2/] A5 = A1 + A4, A6 = A2 + A4, A7 = A1 + A2 + A4.

[3/] $\sigma_T = \sqrt{\sigma_1^2 + \sigma_2^2 + \sigma_3^2}$ = percent variation in measured concentration of SO_2, calculated at a mean concentration of 380 µg/m^3.

[4/] MSE (%) = $\sqrt{\sigma_T^2 + \tau^2}$

DATA PRESENTATION

A reported value whose precision and accuracy (bias) are unknown is of little, if any, worth. The actual error of a reported value--that is, the magnitude and sign of its deviation from the true value--is usually unknown. Limits to this error, however, can usually be inferred, with some risk of being incorrect, from the precision of the measurement process by which the reported value was obtained and from reasonable limits to the possible bias of the measurement process. The bias, or systematic error, of a measurement process is the magnitude and direction of its tendency to measure something other than what was intended; its precision refers to the closeness or dispersion of successive independent measurement generated by repeated applications of the process under specified conditions, and its accuracy is determined by the closeness to the true value characteristic of such measurements.

Precision and accuracy are inherent characteristics of the measurement process employed and not of the particular end result obtained. From experience with a particular measurement process and knowledge of its sensitivity to uncontrolled factors, one can often place reasonable bounds on its likely systematic error (bias). This has been done in the model for the measured concentration as indicated in Table 13. It is also necessary to know how well the particular value in hand is likely to agree with other values that the same measurement process might have provided in this instance or might yield on measurements of the same magnitude on another occasion. Such information is provided by the estimated standard deviation of the reported value, which measures (or is an index of) the characteristic disagreement of repeated determinations of the same quantity by the same method and thus serves to indicate the precision (strictly, the imprecision) of the reported value.

A reported result should be qualified by a quasi-absolute type of statement that places bounds on its systematic error and a separate statement of its standard deviation, or of an upper bound thereto, whenever a reliable determination of such value is available. Otherwise, a computed value of the standard deviation should be given together with a statement of the number of degrees of freedom on which it is based.

As an example, consider strategy AO in Table 13. Here, the assumed standard deviation and bias for a true SO_2 concentration of 380 $\mu g\ SO_2/m^3$ are σ_T = 19 $\mu g\ SO_2/m^3$ (5.0% of 380 $\mu g/m^3$) and τ = -15 $\mu g\ SO_2/m^3$, respectively. The results would be reported as the measured concentration $(\mu g\ SO_2/m^3)_m$ minus the bias and with the following 2σ limits along with the audit level and lot size N; e.g.,

$$(\mu g\ SO_2/m^3)_m + 15 \pm 38,\ n = 7,\ N = 100.$$

For concentration other than 380 μg SO_2/m^3, the overall standard deviation is obtained by

$$\sigma_T(\%) = \sqrt{\sigma_1^2 + \sigma_2^2 + \sigma_3^2}, \text{ and}$$

$$\sigma_T(\mu g/m^3) = \sigma_T(\%) \times \overline{\mu g\ SO_2/m^3}.$$

PERSONNEL REQUIREMENTS

Personnel requirements as described here are in terms of the pararosaniline method only. It is realized that these requirements may be only a minor factor in the overall requirements from a systems point of view where several measurement methods are of concern simultaneously.

Training and Experience

Director - The director or one of the professional-level employees, in addition to formal training in chemistry, should have a basic understanding of statistics as used in quality control. He should be able to perform calculations, such as the mean and standard deviation, required to define data quality. The importance of and requirements for performing independent and random checks as part of the auditing process must be understood. Three references which treat the above-mentioned topics are listed below:

Probability and Statistics for Engineers, Irvin Miller and John E. Freund, published by Prentice-Hall, Inc., Englewood, N. J., 1965.

Introductory Engineering Statistics, Irwin Guttman and S. S. Wilks, published by John Wiley and Sons, Inc., New York, N. Y., 1965.

The Analysis of Management Decisions, William T. Morris, published by Richard D. Irwin, Inc., Homewood, Illinois, 1964.

Operator - There are or can be two levels of operation involved in the manual pararosaniline method.

First, an operator or chemist involved in the reagent preparation or analysis should have formal training in chemistry. A person with a technical or community college background in chemistry with on-the-job experience and close supervision from an experienced chemist could adequately prepare reagents and analyze SO_2 samples.

Field operations involve sample collection and handling only and require no high-level skills. A high school graduate with proper supervision and on-the-job training can become effective at this level in a very short time.

An effective on-the-job training program could be as follows:

(1) Observe experienced operator perform the different tasks in the measurement process.

(2) Study the operational manual of this document and use it as a guide for performing the operations.

(3) Perform operations under the direct supervision of an experienced operator.

(4) Perform operations independently but with a high level of quality control checks utilizing the technique described in the section on Operator Proficiency Evaluation Procedures below to encourage high quality work.

Another alternative would be to have the operator attend an appropriate basic training course sponsored by EPA.

OPERATOR PROFICIENCY EVALUATION PROCEDURES

One technique which may be useful for early training and qualification of operators is a system of rating the operators as indicated below.

Various types of violations (e.g., invalid sample resulting from operator carelessness, failure to maintain records, use of improper equipment, or calculation error) would be assigned a number of demerits depending upon the relative consequences of the violation. These demerits could then be summed over a fixed period of time of one week, month, etc., and a continuous record maintained. The mean and standard deviation of the number of demerits per week can be determined for each operator and a quality control chart provided for maintaining a record of proficiency of each operator and whether any changes in this level have occurred. In comparing operators, it is necessary to assign demerits on a per unit work load basis in order that the inferences drawn from the chart be consistent. *It is not necessary or desirable for the operator to be aware of this form of evaluation. The supervisor should use it as a means of determining when and what kind of instructions and/or training is needed.*

A sample QC chart is given in Figure 23 below. This chart assumes that the mean and standard deviation of the number of demerits per week, are 5 and 1, respectively. After several operators have been evaluated for a few weeks, the limits can be checked to determine if they are both reasonable and effective in helping to improve and/or maintain the quality of the air qulaity measurement.

The limits should be based on the operators whose proficiency is average or slightly better than average. Deviations outside the QC limits, either above or below, should be considered in evaluating the operators. Identifying those operators whose proficiency may have improved is just as important as knowing those operators whose proficiency may have decreased.

The above procedure may be extended to an entire monitoring network (system). With appropriate definitions of work load, a continuous record may be maintained of demerits assigned to the system. This procedure might serve as an incentive for teamwork, making suggestions for improved operation procedures, etc.

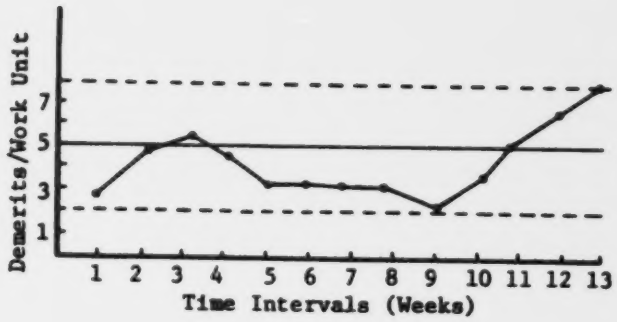

Figure 23: Sample QC Chart for Evaluating Operator Proficiency

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2. F. P. Scaringelli, B. E. Saltzman, and S. A. Frey, "Spectrophotometric Determination of Atmospheric Sulfur Dioxide," Analytical Chemistry 39, page 1709, December 1967.

3. Metronics Dynacal Permeation Tubes, Product Bulletin No. 20-70, Metronics Associates, Inc., Palo Alto, Calif. 94304.

4. F. P. Scaringelli et al., "Preparation of Known Concentrations of Gases and Vapors with Permeation Devices Calibrated Gravimetrically," Analytical Chemistry 42 (8), July 1970, pp. 871-876.

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6. H. C. McKee et al., "Collaborative Study of Reference Method for Determination of Sulfur Dioxide in the Atmosphere (Pararosaniline Method)," Southwest Research Institute, Contract CPA-70-40, SwRI Project 21-2811, San Antonio, Texas, September 1971.

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APPENDIX

REFERENCE METHOD FOR THE DETERMINATION OF SULFUR DIOXIDE IN THE ATMOSPHERE (PARAROSANILINE METHOD)

Reproduced from Appendix A, "National Primary and Secondary Ambient Air Quality Standards," *Federal Register*, Vol 36, No. 84, Part II, Friday, April 30, 1971.

APPENDIX A—REFERENCE METHOD FOR THE DETERMINATION OF SULFUR DIOXIDE IN THE ATMOSPHERE (PARAROSANILINE METHOD)

1 *Principle and Applicability.* 1.1 Sulfur dioxide is absorbed from air in a solution of potassium tetrachloromercurate (TCM). A dichlorosulfitomercurate complex, which resists oxidation by the oxygen in the air, is formed (*1, 2*). Once formed, this complex is stable to strong oxidants (e.g., ozone, oxides of nitrogen). The complex is reacted with pararosaniline and formaldehyde to form intensely colored pararosaniline methyl sulfonic acid (*3*). The absorbance of the solution is measured spectrophotometrically.

1.2 The method is applicable to the measurement of sulfur dioxide in ambient air using sampling periods up to 24 hours.

2 *Range and Sensitivity.* 2.1 Concentrations of sulfur dioxide in the range of 25 to 1,050 $\mu g/m^3$ (0.01 to 0.40 p.p.m.) can be measured under the conditions given. One can measure concentrations below 25 $\mu g/m^3$ by sampling larger volumes of air, but only if the absorption efficiency of the particular system is first determined. Higher concentrations can be analyzed by using smaller gas samples, a larger collection volume, or a suitable aliquot of the collected sample. Beer's Law is followed through the working range from 0.03 to 1.0 absorbance units (0.8 to 27 μg of sulfite ion in 25 ml. final solution computed as SO_2).

2.2 The lower limit of detection of sulfur dioxide in 10 ml. TCM is 0.75 μg, (based on twice the standard deviation) representing a concentration of 25 $\mu g/m^3 SO_2$ (0.01 p.p.m.) in an air sample of 30 liters.

3 *Interferences.* 3.1 The effects of the principal known interferences have been minimized or eliminated. Interferences by oxides of nitrogen are eliminated by sulfamic acid (*4, 5*), ozone by time-delay (*5*), and heavy metals by EDTA (ethylenediaminetetroacetic acid, disodium salt) and phosphoric acid (*4, 6*). At least 80 μg Fe (III), 10 μg Mn(II), and 10 μg Cr(III) in 10 ml. absorbing reagent can be tolerated in the procedure. No significant interference was found with 10 μg Cu (II) and 22 μg V(V).

4. *Precision, Accuracy, and Stability.* 4.1 Relative standard deviation at the 95 percent confidence level is 4.6 percent for the analytical procedure using standard samples. (*5*)

4.2 After sample collection the solutions are relatively stable. At 22° C. losses of sulfur dioxide occur at the rate of 1 percent per day. When samples are stored at 5° C. for 30 days, no detectable losses of sulfur dioxide occur. The presence of EDTA enhances the stability of SO_2 in solution, and the rate of decay is independent of the concentration of SO_2 (*7*).

5 *Apparatus.*

5.1 *Sampling.*

5.1.1 *Absorber.* Absorbers normally used in air pollution sampling are acceptable for concentrations above 25 $\mu g/m^3$ (0.01 p.p.m.). An all-glass midget impinger, as shown in Figure A1, is recommended for 30-minute and 1-hour samples.

For 24-hour sampling, assemble an absorber from the following parts:

Polypropylene 2-port tube closures, special manufacture (available from Bel-Art Products, Pequannock, N.J.).

Glass impingers, 6 mm. tubing, 6 inches long, one end drawn to small diameter such that No. 79 jewelers will pass through, but No. 78 jewelers will not. (Other end fire polished.)

Polypropylene tubes, 164 by 32 mm. (Nalgene or equal).

5.1.2 *Pump.* Capable of maintaining an air pressure differential greater than 0.7 atmosphere at the desired flow rate.

5.1.3 *Air Flowmeter or Critical Orifice.* A calibrated rotameter or critical orifice capable of measuring air flow within ±2 percent. For 30-minute sampling, a 22-gauge hypodermic needle 1 inch long may be used as a critical orifice to give a flow of about 1 liter/minute. For 1-hour sampling, a 23-gauge hypodermic needle five-eighths of an inch long may be used as a critical orifice to give a flow of about 0.5 liter/minute. For 24 hour sampling, a 27-gauge hypodermic needle three-eighths of an inch long may be used to give a flow of about 0.2 liter/minute. Use a membrane filter to protect the needle (Figure A1a).

6.2 *Analysis.*

5.2.1 *Spectrophotometer.* Suitable for measurement of absorbance at 548 nm. with an effective spectral band width of less than 15 nm. Reagent blank problems may occur with spectrophotometers having greater spectral band width. The wavelength calibration of the instrument should be verified. If transmittance is measured, this can be converted to absorbance:

$$A = \log_{10}(1/T)$$

6 *Reagents.*

6.1 *Sampling.*

6.1.1 *Distilled water.* Must be free from oxidants.

6.1.2 *Absorbing Reagent [0.04 M Potassium Tetrachloromercurate (TCM).]* Dissolve 10.86 g. mercuric chloride, 0.066 g. EDTA (thylenediaminetetraacetic acid, disodoum salt), and 6.0 g. potassium chloride in water and bring to mark in a 1,000-ml. volumetric flask. (Caution: highly poisonous. If spilled on skin, flush off with water immediately). The pH of this reagent should be approximately 4.0, but it has been shown that there is no appreciable difference in collection efficiency over the range of pH 3 to pH 5 (*7*). The absorbing reagent is normally stable for 6 months. If a precipitate forms, discard the reagent.

6.2 *Analysis.*

6.2.1 *Sulfamic Acid (0.6 percent).* Dissolve 0.6 g. sulfamic acid in 100 ml. distilled water. Prepare fresh daily.

6.2.2 *Formaldehyde (0.2 percent).* Dilute 5 ml. formaldehyde solution (36–38 percent) to 1,000 ml. with distilled water. Prepare daily.

6.2.3 *Stock Iodine Solution (0.1 N).* Place 12.7 g. iodine in a 250-ml. beaker; add 40 g. potassium iodide and 25 ml. water. Stir until all is dissolved, then dilute to 1,000 ml. with distilled water.

6.2.4 *Iodine Solution (0.01 N).* Prepare approximately 0.01 N iodine solution by diluting 50 ml. of stock solution to 500 ml. with distilled water.

6.2.5 *Starch Indicator Solution.* Triturate 0.4 g. soluble starch and 0.002 g. mercuric iodide (preservative) with a little water, and add the paste slowly to 200 ml. boiling water. Continue boiling until the solution is clear; cool, and transfer to a glass-stoppered bottle.

6.2.6 *Stock Sodium Thiosulfate Solution (0.1 N).* Prepare a stock solution by dissolving 25 g. sodium thiosulfate ($Na_2S_2O_3 \cdot 5H_2O$) in 1,000 ml. freshly boiled, cooled, distilled water and add 0.1 g. sodium carbonate to the solution. Allow the solution to stand 1 day before standardizing. To standardize, accurately weigh, to the nearest 0.1 mg., 1.5 g. primary standard potassium iodate dried at 180° C. and dilute to volume in a 500-ml. volumetric flask. To a 500-ml. iodine flask, pipet 50 ml. of iodate solution. Add 2 g. potassium iodide and 10 ml. of 1 N hydrochloric acid. Stopper the flask. After 5 minutes, titrate with stock thiosulfate solution to a pale yellow. Add 5 ml. starch indicator solution and continue the titration until the blue color disappears. Calculate the normality of the stock solution:

$$N = \frac{W}{M} \times 2.80$$

N = Normality of stock thiosulfate solution.

M = Volume of thiosulfate required, ml.

W = Weight of potassium iodate, grams.

$$2.80 = \frac{10^3 (\text{conversion of g. to mg.}) \times 0.1 (\text{fraction iodate used})}{35.67 (\text{equivalent weight of potassium iodate})}$$

6.2.7 *Sodium Thiosulfate Titrant (0.01 N).* Dilute 100 ml. of the stock thiosulfate solution to 1,000 ml. with freshly boiled distilled water.

Normality = Normality of stock solution × 0.100.

6.2.8 *Standardize Sulfite Solution for Preparation of Working Sulfite-TCM Solution.* Dissolve 0.3 g. sodium metabisulfite ($Na_2S_2O_5$) or 0.40 g. sodium sulfite (Na_2SO_3) in 500 ml. of recently boiled, cooled, distilled water. (Sulfite solution is unstable; it is therefore important to use water of the highest purity to minimize this instability.) This solution contains the equivalent of 320 to 400 μg/ml. of SO_2. The actual concentration of the solution is determined by adding excess iodine and back-titrating with standard sodium thiosulfate solution. To back-titrate, pipet 50 ml. of the 0.01 N iodine into each of two 500-ml. iodine flasks (A and B). To flask A (blank) add 25 ml. distilled water, and to flask B (sample) pipet 25 ml. sulfite solution. Stopper the flasks and allow to react for 5 minutes. Prepare the working sulfite-TCM Solution (6.2.9) at the same time iodine solution is added to the flasks. By means of a buret containing standardized 0.01 N thiosulfate, titrate each flask in turn to a pale yellow. Then add 5 ml. starch solution and continue the titration until the blue color disappears.

6.2.9 *Working Sulfite-TCM Solution.* Pipet accurately 2 ml. of the standard solution into a 100 ml. volumetric flask and bring to mark with 0.04 M TCM. Calculate the concentration of sulfur dioxide in the working solution:

$$\mu g\ SO_2/ml. = \frac{(A - B)(N)(32{,}000)}{25} \times 25 \times 0.02$$

A = Volume thiosulfate for blank, ml.

B = Volume thiosulfate for sample, ml.

N = Normality of thiosulfate titrant.

32,000 = Milliequivalent wt. of SO_2, μg.

25 = Volume standard sulfite solution, ml.

0.02 = Dilution factor.

This solution is stable for 30 days if kept at 5° C. (refrigerator). If not kept at 5° C., prepare daily.

6.2.10 *Purified Pararosaniline Stock Solution (0.2 percent nominal).*

6.2.10.1 *Dye Specifications.* The pararosaniline dye must meet the following performance specifications: (1) the dye must have a wavelength of maximum absorbance at 540 nm. when assayed in a buffered solution of 0.1 M sodium acetate-acetic acid; (2) the absorbance of the reagent blank, which is temperature-sensitive (0.015 absorbance unit/°C), should not exceed 0.170 absorbance unit at 22° C. with a 1-cm. optical path length, when the blank is prepared according to the prescribed analytical procedure and to the specified concentration of the dye; (3) the calibration curve (Section 8.2.1) should have a slope of 0.030±0.002 absorbance units/μg. SO_2 at this path length when the dye is pure and the sulfite solution is

properly standardized.

6.2.10.3 *Preparation of Stock Solution.* A specially purified (99–100 percent pure) solution of pararosaniline, which meets the above specifications, is commercially available in the required 0.20 percent concentration (Harleco*). Alternatively, the dye may be purified, a stock solution prepared and then assayed according to the procedure of Scaringelli, et al. (*4*)

6.2.11 *Pararosaniline Reagent.* To a 250-ml. volumetric flask, add 20 ml. stock pararosaniline solution. Add an additional 0.3 ml. stock solution for each percent the stock assays below 100 percent. Then add 25 ml. 3 M phosphoric acid and dilute to volume with distilled water. This reagent is stable for at least 9 months.

7. *Procedure.*

7.1 *Sampling.* Procedures are described for short-term (30 minutes and 1 hour) and for long-term (24 hours) sampling. One can select different combinations of sampling rate and time to meet special needs. Sample volumes should be adjusted, so that linearity is maintained between absorbance and concentration over the dynamic range.

7.1.1 *30-Minute and 1-Hour Samplings.* Insert a midget impinger into the sampling system, Figure A1. Add 10 ml. TCM solution to the impinger. Collect sample at 1 liter/minute for 30 minutes, or at 0.5 liter/minute for 1 hour, using either a rotameter, as shown in Figure A1, or a critical orifice, as shown in Figure A1a, to control flow. Shield the absorbing reagent from direct sunlight during and after sampling by covering the impinger with aluminum foil, to prevent deterioration. Determine the volume of air sampled by multiplying the flow rate by the time in minutes and record the atmospheric pressure and temperature. Remove and stopper the impinger. If the sample must be stored for more than a day before analysis, keep it at 5° C. in a refrigerator (see 4.3).

7.1.2 *24-Hour Sampling.* Place 50 ml. TCM solution in a large absorber and collect the sample at 0.2 liter/minute for 24 hours from midnight to midnight. Make sure no entrainment of solution results with the impinger. During collection and storage protect from direct sunlight. Determine the total air volume by multiplying the air flow rate by the time in minutes. The correction of 24-hour measurements for temperature and pressure is extremely difficult and is not ordinarily done. However, the accuracy of the measurement will be improved if meaningful corrections can be applied. If storage is necessary, refrigerate at 5° C. (see 4.3).

7.2 *Analysis.*

7.2.1 *Sample Preparation.* After collection, if a precipitate is observed in the sample, remove it by centrifugation.

7.2.1.1 *30-Minute and 1-Hour Samples.* Transfer the sample quantitatively to a 25-ml. volumetric flask; use about 5 ml. distilled water for rinsing. Delay analyses for 30 minutes to allow any ozone to decompose.

7.2.1.2 *24-Hour Sample.* Dilute the entire sample to 50 ml. with absorbing solution. Pipet 5 ml. of the sample into a 25-ml. volumetric flask for chemical analyses. Bring volume to 10 ml. with absorbing reagent. Delay analyses for 30 minutes to allow any ozone to decompose.

7.2.2 *Determination.* For each set of determinations prepare a reagent blank by adding 10 ml. unexposed TCM solution to a 25-ml. volumetric flask. Prepare a control solution by adding 2 ml. of working sulfite-TCM solution and 8 ml. TCM solution to a 25-ml. volumetric flask. To each flask containing either sample, control solution, or reagent blank, add 1 ml. 0.6 percent sulfamic acid and allow to react 10 minutes to destroy the nitrite from oxides of nitrogen. Accurately pipet in 2 ml. 0.2 percent formaldehyde solution, then 5 ml. pararosaniline solution. Start a laboratory timer that has been set for 30 minutes. Bring all flasks to volume with freshly boiled and cooled distilled water and mix thoroughly. After 20 minutes and before 60 minutes, determine the absorbances of the sample (denote as A), reagent blank (denote as A_o) and the control solution at 548 nm. using 1-cm. optical path length cells. Use distilled water, not the reagent blank, as the reference. (NOTE: This is important because of the color sensitivity of the reagent blank to temperature changes which can be induced in the cell compartment of a spectrophotometer.) Do not allow the colored solution to stand in the absorbance cells, because a film of dye may be deposited. Clean cells with alcohol after use. If the temperature of the determinations does not differ by more than 3° C. from the calibration temperature (8.2), the reagent blank should be within 0.03 absorbance unit of the y-intercept of the calibration curve (8.2). If the reagent blank differs by more than 0.03 absorbance unit from that found in the calibration curve, prepare a new curve.

7.2.3 *Absorbance Range.* If the absorbance of the sample solution ranges between 1.0 and 3.0, the sample can be diluted 1:1 with a portion of the reagent blank and read within a few minutes. Solutions with higher absorbance can be diluted up to sixfold with the reagent blank in order to obtain onscale readings within 10 percent of the true absorbance value.

8. *Calibration and Efficiencies.*

8.1 *Flowmeters and Hypodermic Needle.* Calibrate flowmeters and hypodermic needle (*8*) against a calibrated wet test meter.

8.2 *Calibration Curves.*

8.2.1 *Procedure with Sulfite Solution.* Accurately pipet graduated amounts of the working sulfite-TCM solution (6.2.9) (such as 0, 0.5, 1, 2, 3, and 4 ml.) into a series of 25-ml. volumetric flasks. Add sufficient TCM solution to each flask to bring the volume to approximately 10 ml. Then add the remaining reagents as described in 7.2.2. For maximum precision use a constant-temperature bath. The temperature of calibration must be maintained within ±1° C. and in the range of 20° to 30° C. The temperature of calibration and the temperature of analysis must be within 2 degrees. Plot the absorbance against the total concentration in μg. SO_2 for the corresponding solution. The total μg. SO_2 in solution equals the concentration of the standard (Section 6.2.9) in μg. SO_2/ml. times the ml. sulfite solution added (μg. SO_2 = μg./ml. SO_2 × ml. added). A linear relationship should be obtained, and the y-intercept should be within 0.03 absorbance unit of the zero standard absorbance. For maximum precision determine the line of best fit using regression analysis by the method of least squares. Determine the slope of the line of best fit, calculate its reciprocal and denote as B_s. B_s is the calibration factor. (See Section 6.2.10.1 for specifications on the slope of the calibration curve). This calibration factor can be used for calculating results provided there are no radical changes in temperature or pH. At least one control sample containing a known concentration of SO_2 for each series of determinations, is recommended to insure the reliability of this factor.

8.2.2 *Procedure with SO_2 Permeation Tubes.*

8.2.2.1 *General Considerations.* Atmospheres containing accurately known amounts of sulfur dioxide at levels of interest can be prepared using permeation tubes. In the systems for generating these atmospheres, the permeation tube emits SO_2 gas at a known, low, constant rate, provided the temperature of the tube is held constant (±0.1° C.) and provided the tube has been accurately calibrated at the temperature of use. The SO_2 gas permeating from the tube is carried by a low flow of inert gas to a mixing chamber where it is accurately diluted with SO_2-free air to the level of interest and the sample taken. These systems are shown schematically in Figures A2 and A3 and have been described in detail by O'Keeffe and Ortman (*9*), Scaringelli, Frey, and Saltzman (*10*), and Scaringelli, O'Keeffe, Rosenberg, and Bell (*11*).

8.2.2.2 *Preparation of Standard Atmospheres.* Permeation tubes may be prepared or purchased. Scaringelli, O'Keeffe, Rosenberg, and Bell (*11*) give detailed, explicit directions for permeation tube calibration. Tubes with a certified permeation rate are available from the National Bureau of Standards. Tube permeation rates from 0.2 to 0.4 μg./minute inert gas flows of about 50 ml./minute and dilution air flow rates from 1.1 to 15 liters/minutes conveniently give standard atmospheres containing desired levels of SO_2 (25 to 280 μg./m.³; 0.01 to 0.15 p.p.m. SO_2). The concentration of SO_2 in any standard atmosphere can be calculated as follows:

$$C = \frac{P \times 10^9}{R_s + R_i}$$

Where:

C = Concentration of SO_2, μg./m.³ at reference conditions.

P = Tube permeation rate, μg./minute.

R_s = Flow rate of dilution air, liter/minute at reference conditions.

R_i = Flow rate of inert gas, liter/minute at reference conditions.

8.2.2.3 *Sampling and Preparation of Calibration Curve.* Prepare a series (usually six) of standard atmospheres containing SO_2 levels from 25 to 300 μg. SO_2/m.³. Sample each atmosphere using similar apparatus and taking exactly the same air volume as will be done in atmospheric sampling. Determine absorbances as directed in 7.2. Plot the concentration of SO_2 in μg./m.³ (x-axis), against $A - A_o$ values (y-axis), draw the straight line of best fit and determine the slope. Alternatively, regression analysis by the method of least squares may be used to calculate the slope. Calculate the reciprocal of the slope and denote as B_s.

8.3 *Sampling Efficiency.* Collection efficiency is above 98 percent; efficiency may fall off, however, at concentrations below 25 μg./m.³. (*12, 13*)

9. *Calculations.*

9.1 *Conversion of Volume.* Convert the volume of air sampled to the volume at reference conditions of 25° C. and 760 mm. Hg. (On 24-hour samples, this may not be possible.)

$$V_s = V \times \frac{P}{760} \times \frac{298}{t + 273}$$

V_s = Volume of air at 25° C. and 760 mm. Hg, liters.

V = Volume of air sampled, liters.

P = Barometric pressure, mm. Hg.

t = Temperature of air sample, °C.

9.2 *Sulfur Dioxide Concentration.*

9.2.1 When sulfite solutions are used to prepare calibration curves, compute the concentration of sulfur dioxide in the sample:

$$\mu g.\ SO_2/m.^3 = \frac{(A - A_o)\ (10^9)\ (B_s)}{V_s} \times D$$

A = Sample absorbance.

A_o = Reagent blank absorbance.

10^9 = Conversion of liters to cubic meters.

V_s = The sample corrected to 25° C. and 760 mm. Hg, liters.

*Hartmen-Leddon, 60th and Woodland Avenue, Philadelphia, PA 19143.

B_s = Calibration factor, μg./absorbance unit.

D = Dilution factor.

For 30-minute and 1-hour samples, D=1.

For 24-hour samples, D=10.

9.3.3 When SO_2 gas standard atmospheres are used to prepare calibration curves, compute the sulfur dioxide in the sample by the following formula:

$$SO_2, \mu g./m.^3 = (A - A_o) \times B_s$$

A = Sample absorbance.

A_o = Reagent blank absorbance.

B_s = (See 9.3.3.3).

9.3.3 *Conversion of μg./m.³ to p.p.m.* = If desired, the concentration of sulfur dioxide may be calculated as p.p.m SO_2 at reference conditions as follows:

$$\text{p.p.m. } SO_2 = \mu g.\ SO_2/m.^3 \times 3.82 \times 10^{-4}$$

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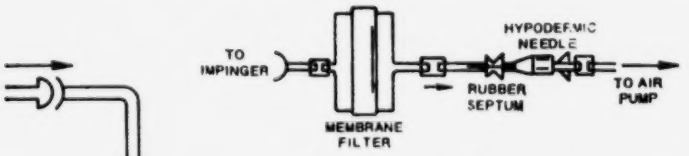

Figure A1a. Critical orifice flow control.

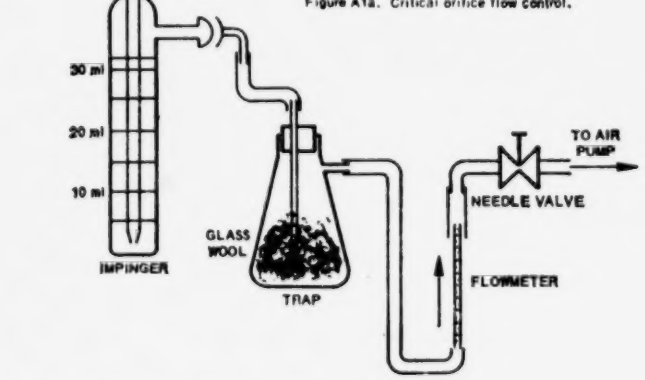

Figure A1. Sampling train.

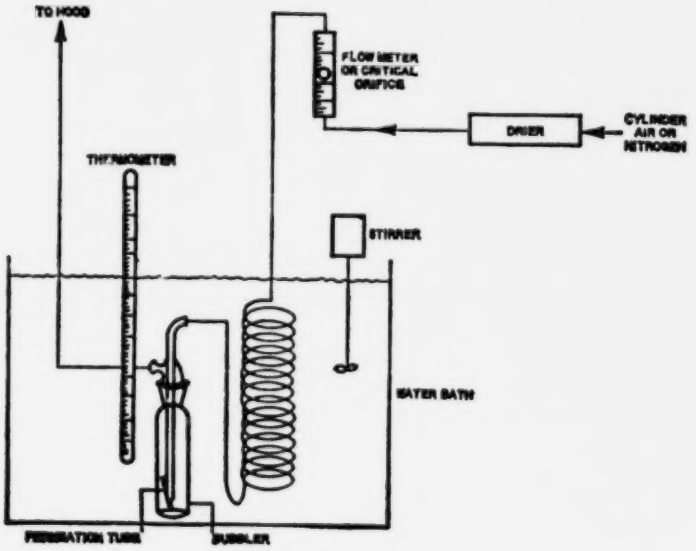

Figure A2. Apparatus for [illegible]

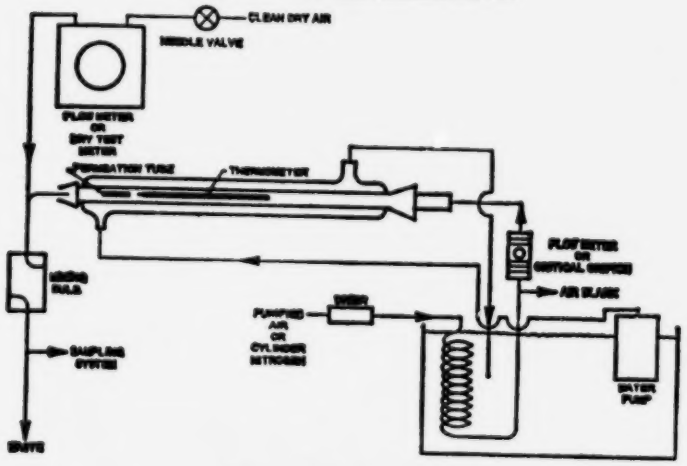

Figure A3. [illegible]